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RECOMMENDED METHODS OF REDUCTION, NEUTRALIZATION, RECOVERY, OR DISPOSAL OF HAZARDOUS WASTE

VOLUME V. NATIONAL DISPOSAL SITE CANDIDATE WASTE STREAM CONSTITUENT PROFILE REPORTS. PESTICIDES AND CYANIDE COMPOUNDS

TRW SYSTEMS GROUP

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

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RECOMMENDED METHODS OF
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Volume V. National Disposal Site Candidate Waste Stream Constituent Profile Reports - Pesticides and Cyanide Compounds

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in:

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

Under Section 212 of Public Law 91-512, the Resource Recovery Act of 1970, the U.S. Environmental Protection Agency is charged with preparing a comprehensive report and plan for the creation of a system of National Disposal Sites for the storage and disposal of hazardous wastes. The overall program is being directed jointly by the Solid and Hazardous Waste Research Laboratory, Office of Research and Development, National Environmental Research Center, Cincinnati, and the Office of Solid Waste Management Programs, Office of Hazardous Materials Control. Section 212 mandates, in part, that recommended methods of reduction, neutralization, recovery, or disposal of the materials be determined. This determination effort has been completed and prepared into this 16-volume study. The 16 volumes consist of profile reports summarizing the definition of adequate waste management and evaluation of waste management practices for over 500 hazardous materials. In addition to summarizing the definition and evaluation efforts, these reports also serve to designate a material as a candidate for a National Disposal Site, if the material meets criteria based on quantity, degree of hazard, and difficulty of disposal. Those materials which are hazardous but not designated as candidates for National Disposal Sites, are then designated as candidates for the industrial or municipal disposal sites.

A. W. Breidenbach, Ph.D., Director
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PROFILE REPORTS ON
HIGHLY CHLORINATED HYDROCARBON PESTICIDES

THE POLYCHLOROCYCLODIENES

Aldrin (13), Chlordane, (484), Dieldrin (149),
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I. GENERAL

Introduction

The polychlorocyclodiene insecticides are highly chlorinated cyclic hydrocarbons with endomethylene structures prepared by the Diels-Alder diene reaction. The development of these insecticides was largely the result of the work of J. Hyman and his associates dating from 1945, although chlordane is said to have been discovered independently by Riemschneider in Germany at about the same period.[0509,1617] The polychlorocyclodiene insecticides are very extensively used for the control of grasshoppers, cotton insects, household insects, and as soil insecticides.

The polychlorocyclodiene insecticides have not fared too well in recent years as their tendencies for growth are being overcome by obsolescence and by attrition owing to the competition from new products which are more economical, less toxic to higher animals, and more readily degradable. The production figures for the aldrin-toxaphene group of insecticides are as follows[0449,1610]:

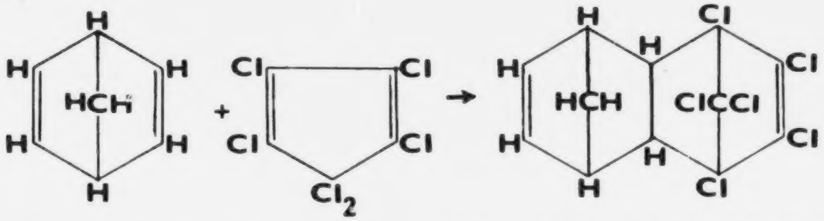
Annual Production (thousand lb)

1960	1961	1962	1963	1964	1965	1966	1967
90,671	103,763	106,276	105,986	105,296	118,832	130,470	120,183

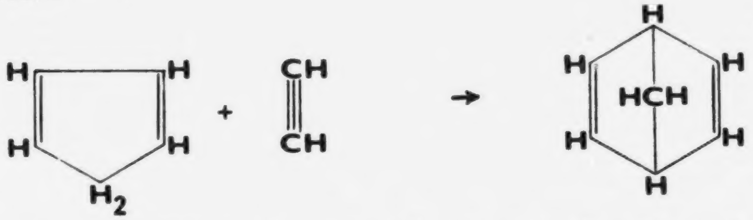
In 1970 only 88,641,000 lb of insecticides of the aldrin-toxaphene group were produced.[1718] The aldrin-toxaphene group includes all five polychlorocyclodiene insecticides discussed in this Profile Report, and toxaphene. The production figures thus illustrate the rise and decline of these pesticides, especially when the total organic pesticides market is still rapidly growing.

Manufacture

Aldrin. The main method of producing aldrin is the reaction of hexachlorocyclopentadiene with an excess of bicyclo-[2.2.1]-2,5-heptadiene at 100 C[1618]:

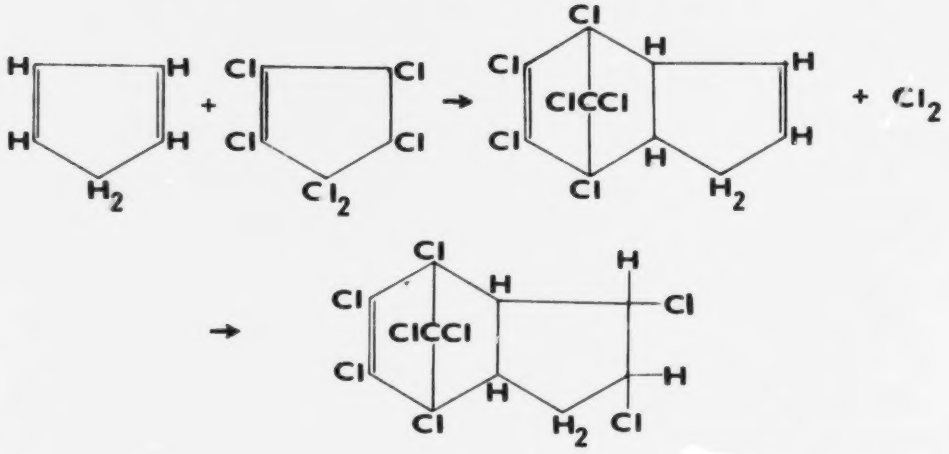


The bicyclo-[2.2.1]-2,5-heptadiene required is obtained by the Diels-Alder reaction between cyclopentadiene and acetylene at 250 to 360 C and 4 to 20 atm pressure[1618]:



Shell Chemical Company at Denver, Colorado, is the only U.S. producer of aldrin.[1718]

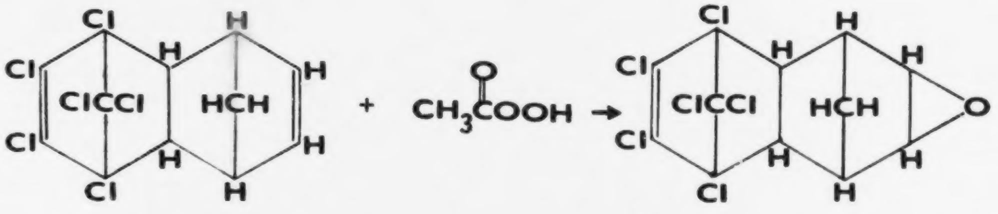
Chlordane. Chlordane is manufactured by the reaction of hexachlorocyclopentadiene with cyclopentadiene at 80 to 90 C to form hexachlorodicyclopentadiene (chlordene), followed by the subsequent chlorination of the chlordene at 50 to 80 C[1618]:



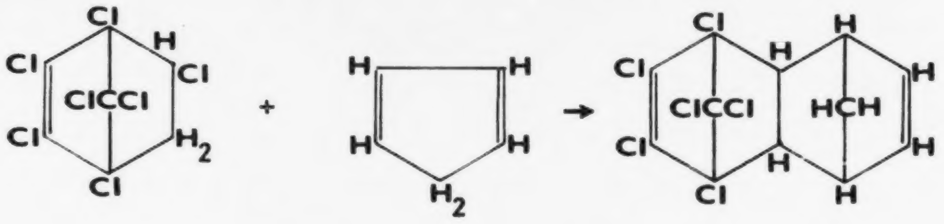
Velsicol Chemical Company at Marshall, Illinois is the only U.S. producer of chlordane.

Dieldrin. Dieldrin is obtained in 90 percent yield by the oxidation of aldrin by organic peracids or hydrogen peroxide in acetic acid. Like aldrin, the only U.S. producer of dieldrin is Shell Chemical Company at Denver, Colorado.

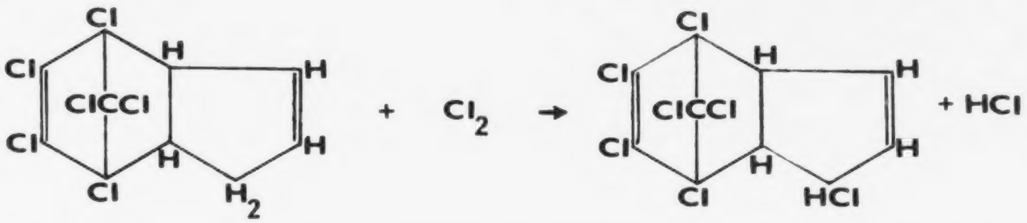
Endrin. Endrin is produced by the oxidation of isodrin with peracetic acid[1617]:



whereas the insecticide isodrin is obtained by the condensation of cyclopentadiene with 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2,5-heptadiene[1618]:



Heptachlor. Heptachlor is produced by the substitutive chlorination of chlordene. The reaction proceeds at low temperatures and in the presence of silica gel or other similar catalysts[1618]:



Like endrin, the only U.S. producer of heptachlor is Velasciol Chemical Company at Memphis, Tennessee.

Uses

Aldrin is a broad spectrum insecticide used for the control of insect pests of fruits, vegetables, cotton, and as a soil insecticide and for soil treatment. Chlordane is used as an agent to control various chewing pests and especially to protect nonmetallic materials from termites under tropical conditions, and also for the control of soil insects and certain pests of vegetable and soil crops. Dieldrin is more stable and residual than aldrin and is used in addition for the control of grasshoppers, insects of public health importance, termites, and for mothproofing. Endrin is especially used for the control of lipidopterous larvae attacking cotton, field, and vegetable crops. It is also used to control the black-currant bud mite, against which all other insecticides are ineffective, and as a zoocide. Heptachlor has much the same spectrum of effectiveness as chlordane and is used to control soil-inhibiting pests such as wireworms and gray sugarbeet weevil, grasshoppers, and also as an insecticidal additive to seed disinfectants. In recent years the more effective heptachlor is gradually displacing chlordane.[0509,1618]

Sources and Types of Pesticide Wastes

The sources of pesticide wastes may include the following[0620]: (1) pesticide manufacturers; (2) pesticide formulators; (3) pesticide wholesalers; (4) professional applicators; (5) cooperage facilities that recondition drum; (6) agricultural users; (7) government facilities that store, transport, and use pesticides; (8) urban and suburban home and garden users; (9) commercial and industrial processes including those from rug and fabric treatment facilities manufacturing plants, hospital, etc.

In general, pesticide wastes can be classified as either diluted or concentrated wastes. Diluted pesticide waste include those generated in the waste waters of the manufacturers, formulators, agricultural runoffs, and possibly spent caustic solutions used to clean empty pesticide containers. Concentrated pesticide wastes include any unused or contaminated pesticides, pesticide materials left in containers after emptying, sludges formed in treating waste water containing pesticides, sawdust or straw used to soak up accidental pesticide spills.

Polychlorocyclodiene pesticides appear as waste stream constituents in varied forms and compositions. Typical waste streams containing heptachlor, chlordane, dieldrin and endrin are as follows:

Aldrin containing liquid wastes from spill cleanup and floor washings;

Solid wastes containing 0.5 percent aldrin;

Aqueous waste containing dieldrin in the ppm range;

Solid waste containing 0.5 percent dieldrin;

Liquid waste containing approximately 12 percent NaCl, 2 percent NaOCl, 2 percent NaOH and chlordane in the ppm range;

Solid waste containing 0.5 percent chlordane;

Aqueous waste containing 0.5 ppm heptachlor;

Solid waste containing 0.5 percent heptachlor;

Aqueous slurry containing 2.5 percent heptachlor and 10 percent diatomoceous earth;

Solid waste containing 0.5 percent endrin.

More detailed information relating to the forms and quantities of polychlorocyclodiene pesticides is presented in Volume titled "Waste Forms and Quantities".

Physical and Chemical Properties

The physical and chemical properties of aldrin, chlordane, dieldrin, endrin, and heptachlor are included in the attached worksheets. It should be noted that dieldrin is the epoxide of aldrin, and endrin is the endo, endo-isomer of dieldrin. Chlordane exists in two isomeric forms, the α-trans and the β-cis.

2. TOXICOLOGY

The symptoms of polychlorocyclodiene pesticide poisoning in insects resemble those of DDT, and are displayed by hypersensitivity, hyperactivity with violent bursts of convulsions, and finally complete prostration with convulsive movements. However, the site of these disturbances lies in the ganglia of the central nervous system rather than in the peripheral nerves as with DDT. The precise biochemical lesion responsible for the toxic action of the polychlorocyclodiene insecticides is unknown, but it has been theorized that it is related to the absorption and critical fit of the active compounds into the pores of nerve membranes to produce convulsant action. The polychlorocyclodienes are all readily absorbed by the insect cuticle.[0509]

All the polychlorocylodiene insecticides are toxic to higher animals and poisoning could be caused by ingestion, inhalation, or absorption through the skin. The use of aldrin, dieldrin, and endrin is not permitted in the Soviet Union.[1618]

Acute poisoning of aldrin may cause renal damage, tremors, ataxia, and convulsions followed by central nervous system depression, respiratory failure, and death. Prolonged exposure may lead to hepatic damage.[1492]

The fatal dose of chlordane to man is unknown, but has been estimated to be between 6 and 60 gm. Acute poisoning may be characterized by irritability, convulsions, and deep depression. The dangerous chronic dose in man is also unknown, although it has been established that continued ingestion causes degenerative changes in the liver.[0766,1492]

The effects of dieldrin and aldrin are similar both quantitatively and qualitatively in animals as well as in man. Persons exposed to oral dosages which exceed 10 mg/kg frequently became acutely ill. Symptoms may appear within 20 minutes and in no instance has a latent period of more than 12 hours been confirmed.[0766]

Endrin exhibits toxic effects similar to aldrin and dieldrin.[1492]

Acute poisoning of heptachlor may be characterized by tremors, ataxia, convulsions, renal damage, respiratory failure, and death, the latter resulting from ingestion of or skin contamination with 1 to 3 g. There are also some indications that like chlordane, chronic poisoning with small dosages may cause hepatic damage.[1492] Oxidation of heptachlor leads to the more toxic epoxide, and the reaction takes place readily in animals and possibly in insects. It is probable that the effect of heptachlor is based on the reaction of its epoxide with the vital systems in animals and insects.

The acute oral and dermal LD_{50} values of the polychlorocyclodiene insecticides to rats have all been well established (Table 1). The acute oral LD_{50} values range from 8 mg/kg body weight for endrin to 430 mg/kg body weight for chlordane, and because all the polychlorocyclodiene insecticides are readily absorbed through the skin, their dermal LD_{50} values are usually less than twice the corresponding acute oral LD_{50} values.[1277] The American Conference of Governmental Industrial Hygienists 1971 recommended Threshold Limit Values (TLV) for the compounds in mg/M^3 of air are [225]: aldrin, 0.25; chlordane, 0.5; dieldrin, 0.25; endrin, 0.1; heptachlor, 0.5.

The 48-hour Median Tolerance Limits (TL_m) for the polychlorocyclodiene insecticides for various types of fresh water organisms have been established by the Federal Water Pollution Control Administration (Table 2). These data are indicative of the water pollution hazards associated with the use of the polychlorocyclodiene insecticides.

The oxidative conversion of aldrin and heptachlor to their much more stable epoxides is an important reaction in both plant and animal tissues.

TABLE 1

ACUTE ORAL AND DERMAL LD_{50} VALUES OF POLYCHLOROCYCLODIENE INSECTICIDES FOR WHITE RATS[1277]

Insecticides	Oral LD_{50} (mg/kg)		Dermal LD_{50} (mg/kg)	
	Males	Females	Males	Females
Aldrin	39	60	98	98
Chlordane	335	430	840	690
Dieldrin	46	46	90	60
Endrin	18	8	18	15
Heptachlor	100	162	195	250

TABLE 2

48-HOUR TL_m VALUES FROM BIOASSY
(in micrograms per liter)[536]

Insecticides	Stream Invertebrate Species	TL_m	Cladocerans Species	TL_m	Fish Species	TL_m	Gammarus Lacustris TL_m
Aldrin	P. Californica	8	D. Pulex	28	Rainbow t.	3	12,000
Chlordane	P. Californica	55	S. Serrulatus	20	Rainbow t.	10	80
Dieldrin	P. Californica	1.3	D. Pulex	240	Bluegill	3.4	1,000
Endrin	P. Californica	0.8	D. Pulex	20	Bluegill	0.2	4.7
Heptachlor	P. Badia	4	D. Pulex	42	Rainbow t.	9	100

The half-lives of aldrin or heptachlor on alfalfa are less than one day, but that of dieldrin is 7 days, and of heptachlor epoxide is 8 days. Heptachlor fed to animals is concentrated about 20 times and stored as heptachlor epoxide. All the other polychlorocyclodiene insecticides are also stored in the body fat in various levels.[0449] Epoxidation and accumulation in animal tissues of these insecticides lead to undesirable biological magnification in food chain organisms, thus posing serious problems of environmental contamination even when they are only present in small quantities.

3. OTHER HAZARDS

The polychlorocyclodienes are relatively chemically stable compounds. However, a small amount of hydrogen chloride is given off when chlordane is acted on by water, and this must be taken into consideration when it is stored in a metal container. Moist chlordane strongly corrodes metals, and small amounts of epichlorohydrin are often added to chlordane for the purpose of tying up the hydrogen chloride evolved in storage.[1618]

The fire hazards associated with the polychlorocylodiene insecticides usually depend only on the solvents employed in their formulation. When heated to decomposition, however, they emit highly toxic fumes of hydrogen chloride and other chlorinated products.[0766]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Since all the polychclorocyclodiene insecticides are toxic to man by inhalation, ingestion,or skin contact, great care must be exercised in their handling. The use of rubber gloves, goggles, a respirator, and full protective clothing is recommended in the handling and application of these insecticides, and any material spilled on the skin should be immediately removed with plenty of water and soap. If clothing has been contaminated, it should be removed as soon as possible and the skin washed as above.

The polychlorocyclodiene insecticides should be stored in cool, dry, well-ventilated places, and away from any area where the fire hazard may be acute. Outside or detached storage is preferred. Proper warning signs should be posted in storage areas.

Aldrin, dieldrin, and endrin are classified as Class B poisons by the Department of Transportation, and the rules and regulations governing their transporation are given in the Code of Federal Regulations (CFR) Title 49-Transportation, Parts 71-90.[0278] Chlordane and heptachlor are less toxic and not classified by the Department of Transportation and no specific rules governing their transportation are prescribed.

The National Agricultural Chemicals Association has established a Pesticide Safety Team Network with Area Coordinators throughout the country to provide nationwide 24-hour service . The network became operational on March 9, 1970 (with a central telephone number-[513]-916-4300) and should be consulted in all cases of accidents, spills, leakage, fires, and other types of disasters involving the polychlorocyclodiene insecticides.

Disposal/Reuse

Contaminated or degraded polychclorocyclodiene insecticides could not be practically considered for reprocessing. The safe disposal of the insecticides is defined in terms of provisional limits in the atmosphere and a potable water source/or marine habitat. The provisional limits are as follows:

Contaminant in Air	Provisional Limits	Basis for Recommendation
Aldrin	0.0025 mg/M^3	0.01 TLV
Chlordane	0.005 mg/M^3	"
Dieldrin	0.0025 mg/M^3	"
Endrin	0.001 mg/M^3	"
Heptachlor	0.005 mg/M^3	"

Contaminant in Water and Soil	Provisional Limits	Basis for Recommendation
Aldrin	0.012 ppm (mg/l)	Stokinger and Woodward Method
Chlordane	0.025 ppm (mg/l)	Stokinger and Woodward Method
Dieldrin	0.012 ppm (mg/l)	Stokinger and Woodward Method
Endrin	0.005 ppm (mg/l)	Stokinger and Woodward Method
Heptachlor	0.025 ppm (mg/l)	Stokinger and Woodward Method

The point source strategy of monitoring waste effluents is suggested as the best current solution of minimizing water pollution by the polychlorocyclodiene insecticides.[1612] Analysis of a combination of stream water, mud, and aquatic life is considered as inadequate because of the persistence of these compounds, which makes it difficult to relate the presence of the pesticides to the time and place of their introduction.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Dilute Pesticide Wastes

Option No.1 - Adsorption with Powdered Activated Carbon.* The effectiveness of powdered activated carbon on the removal of polychlorocyclodiene insecticides from water has been reported by Robeck et al,[0441] Sigworth,[1635] and Whitehouse.[0445] Robeck et al investigated initial dieldrin and endrin concentrations in the 0.5 to 10 ppb range and found that final reduction of the pesticide level to 0.25 ppb could be accomplished with powdered activated carbon dosages of 30 to 60 ppm. Sigworth's studies were conducted with initial chlordane concentrations of 50 ppm, and he concluded that 10 ppm carbon dosages in a treatment plant would accomplish over 99 percent removal of chlordane and at least 90 percent removal of most of the pesticides that are extensively used today. Whitehouse investigated the effects of carbon dosage and contact time on aldrin and dieldrin removal from water, with initial aldrin and dieldrin concentrations of 0.0066 ppm and 0.0040 ppm respectively, and showed that over 90 percent removal of pesticides could be obtained after one hour and carbon dosage of 100 ppm in the case of aldrin and 200 ppm in the case of dieldrin. The necessary carbon dosage and the associated degree of removal of heptachlor should be in the same range as those for chlordane. Based on the results of these studies, the addition of powdered activated carbon to a liquid solution followed by stirring and filtration is an adequate method for treating dilute polychlorocyclodiene pesticide wastes.

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* The contaminated carbon could be regenerated in a multi-hearth furnace under a controlled atmosphere at temperatures in excess of 1600 F, so that the adsorbed impurities are voltalized and selectively oxidized from the surface of the carbon.

Option No.2 - Adsorption with Granual Activated-Carbon Beds.* The effectiveness of granular activated-carbon beds to remove dieldrin and endrin from water has been investigated by Robeck et al.[0441] Following passage through two carbon columns, it was found that initial dieldrin concentrations of 4.3 ppb and 0.5 ppb could be reduced to 0.05 ppb and well below 0.01 ppb respectively. Endrin removal was also reported to be over 99 percent. Treatment of waste carbon beds has been practiced by Fisons Pest Control Ltd., in England since 1955,[1035,1631] where 99 percent removal of the pesticides are obtained. The treated effluent is diluted with river water before discharge to the river, and the results of government biological surveys indicated no effects of the discharge on the river. Because of the adequate contact time provided and the fact that it is a well established chemical engineering unit operation, adsorption with granular activated-carbon beds should be considered as one of the most satisfactory methods for treating dilute polychlorocyclodiene pesticide wastes.

Option No.3 - Acid Hydrolysis. Whitehouse reported that below a pH value of 3 the concentration of aldrin and dieldrin in water rapidly decreased.[0445] Aldrin, dieldrin, and endrin have also been reported to undergo decomposition in the presence of acid by Melnikov.[1618] However, based on the limited information available to date, acid hydrolysis could only be considered as a possible treatment method for aldrin, dieldrin, and endrin.

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* The contaminated carbon could be regenerated in a multi-hearth furnace under a controlled atmosphere at temperatures in excess of 1600 F, so that the absorbed impurities are voltalized and selectively oxidized from the surface of the carbon.

Option No.4 - Chemical Oxidation. Buescher et al[0442] examined the effects of various chemical oxidants on aldrin and dieldrin. They concluded that aldrin in saturated aqueous solutions were readily and completely removed by chlorination, potassium permanganate, and ozonation, up to 85 percent removed by aeration, and not removed at all by peroxides. Among the chemical oxidants tested, potassium permanganate was found to be the most efficient and a one mg/liter dosage could result in the complete removal of aldrin in 15 minutes contact time. In the case of dieldrin, the pesticide concentration in saturated solutions was decreased by approximately 80 percent by ozonation and aeration. In a concurrent and independent study,[0445] Whitehouse also found that aldrin and dieldrin were removed by aeration to a significant extent. Robeck et al in 1965[0441] found that chlorine and potassium permanganate at 1 to 5 ppm did not reduce dieldrin or endrin, although ozone doses of 10 ppm did reduce 10 ppb dieldrin in water to 5 ppb. The more recent study by Leigh in 1969[1629] showed that potassium permanganate in 40 mg/liter dosage was effective in removing heptachlor over a wide range in pH and a reasonable length of time, and heptachlor removals of more than 80 percent in less than 5 hr were observed. The same study also indicated that chlorine was much less effective than potassium permanganate in removing heptachlor, whereas endrin was not removed by potassium permanganate, potassium persulfate, or chlorine. Based on the results of these studies, it may be concluded that potassium permanganate addition to waste water is as effective means of removing aldrin and heptachlor, and ozonation could be used for removing aldrin.

Option No.5 - Anaerobic Degradation. The anaerobic degradation of aldrin, dieldrin, endrin, and heptachlor has been investigated by Hill and McCarty.[1628] They concluded that all the polychlorocyclodiene insecticides studied experienced some degradation under suitable anaerobic conditions, and with the exception of dieldrin, the degradation was also more rapid than under the corresponding aerobic conditions. Experiments conducted with thick anaerobic sludge at 95 F and large doses of pesticide mixtures indicated that 40 ppm aldrin added could be completely degraded in 56 days, 150 ppm endrin in 30 days, and 10 ppm heptachlor in 20 minutes, whereas dieldrin showed little or no degradation. Both endrin and heptachlor formed extractable degradation products, but these pesticides and their extractable degradation products together were still less persistent than aldrin under anaerobic conditions. Based on these experimental results, anaerobic degradation with sufficient residence time should be considered as an adequate method for treating dilute aldrin, endrin, or heptachlor wastes.

Option No.6 - Removal by Surface Active Agents. The removal of aldrin and dieldrin from water by the use of surface active agents to produce a foam has been investigated by Whitehouse.[0445] The amount of removal accomplished by foaming with a given dose of surface active agent was found to be increased as the pH decreased. Of the three types of surface active agents tested, alkyl benzene sulfonate (anionic), Dowfax 9N9 (nonionic), and Aerosol C-61 (cationic), the cationic when applied in 7 to 14 mg/liter dosages effected greater than 90 percent removal of both aldrin and dieldrin (when aldrin and dieldrin were initially present in concentrations of 0.02 ppm and 0.035 ppm respectively). The results of these studies demonstrated the value of the process as a near future treatment method for aldrin, dieldrin, and possibly other types of pesticides.

The other treatment processes for the removal of polychlorocyclodiene insecticides from water that have been investigated include adsorption with clay and coagulation and filtration. Whitehouse[0445] showed that the removal of aldrin and dieldrin by adsorption with clay or chemical coagulation was not totally effective and only of the order of 10 to 50 percent. Robeck et al[0441] reported 55 percent removal for dieldrin and 35 percent removal for endrin by coagulation and filtration when the pesticides were initially present in 1 to 10 ppm concentrations. These processes are therefore considered as inadequate methods for treating dilute polychlorocyclodiene pesticide wastes.

Concentrated Pesticide Wastes

Option No.1 - Incineration. The complete and controlled high temperature oxidation of polychlorocyclodiene insecticides in air or oxygen with adequate scrubbing and ash disposal facilities offers the greatest immediate potential for the safe disposal of pesticides. The research on incineration of pesticides conducted by Kennedy et al at Mississippi State University has led to the conclusion that temperatures at or near 1,800 F will be sufficient to degrade 99.5 percent of dieldrin and 99 percent or more of most reagent grade pesticides and commercial pesticide formulations.[0062,0063] It is expected that either a rotary kiln or liquid combustor, depending upon the waste form, followed by secondary combustion and scrubbing would be an acceptable disposal method. Primary combustion should be carried out at a minimum of 1,500 F for at least 0.5 seconds with secondary combustion at a minimum of 2,200 F for at least 1.0 sec. In the case of dieldrin, the volatile products identified from burning of the formulation at 1,650 F include carbon monoxide, carbon dioxide, chlorine and hydrogen chloride. The equilibrium product distributions resulting from the thermal decomposition and combustion of aldrin at atmospheric pressure and three temperatures, 2,190 F (1,200 C), 1,470 F (800 C), 930 F (500 C), have also been computed using the TRW Chemical Analysis Program (Table 3). The results also indicate the possible formation of hydrogen chloride, but that at high air/fuel ratios, complete combustion is approached and both methane and carbon monoxide are only present in small quantities. As the same combustion products will be obtained in the incineration of other polychlorocyclodiene insecticides, an adequate gas clean up system to remove chlorine and hydrogen chloride must be installed to alleviate the air pollution problem. The abatement problem may be simplified by ensuring against elemental chlorine formation through injection of steam or methane into the combustion process. Incineration is also one of the principal means of disposing heptachlor and endrin manufacturing wastes at Velsicol's Memphis, Tennessee plant.[1736] In addition, combustion units designed for the disposal of chlorinated organic wastes and capable of recovering chlorine in the form of usable hydrogen chloride have been developed, and a 7,000 lb/hr plant is now under construction for E. I. du Pont de Nemours & Company in Victoria, Texas by Union Carbide Corporation.[1743]

TABLE 3
EQUILIBRIUM COMPOSITION OF ALDRIN/AIR SYSTEM
(1 ATM PRESSURE) MOLE FRACTION, GAS PHASE *+

Wt % Pesticide	Temp.	CH_4	CO	CO_2	H_2	H_2O	HCl	HCN	N_2	Condensed Phase Graphite Mol/100 G Feed
100	1200 C	-	-	-	1.428-1	-	8.572-1	-	-	3.288
	800 C	9.222-4	-	-	1.411-1	-	8.579-1	-	-	3.286
	500 C	2.256-2	-	-	1.010-1	-	8.765-1	-	-	3.246
70	1200 C	-	1.573.1	-	7.831-2	-	4.708-1	1.978-4	2.933-1	1.991
	800 C	2.730-4	1.502-1	3.220-3	7.679-2	1.508-3	4.731-1		2.948-1	2.003
	500 C	4.302-3	1.572-2	6.191-2	4.409-2	3.357-2	5.178-1	-	3.226-1	2.202
50	1200 C	-	2.396-1	-	4.469-2	-	2.688-1	1.844-4	4.467-1	0.911
	800 C	-	2.259-1	7.280-3	4.371-2	1.291-3	2.711-1	-	4.506-1	0.937
	500 C	1.262-3	2.129-2	1.136-1	2.388-2	2.463-2	3.063-1	-	5.090-1	1.279
20	1200 C	-	5.878-2	1.450-1	2.403-3	1.459-2	1.019-1	-	6.773-1	-
	800 C	-	5.619-2	1.476-1	4.986-3	1.200-2	1.019-1	-	6.773.1	-
	500 C	1.260-4	2.579-2	1.667-1	7.545-3	9.426-3	1.034-1	-	6.871-1	0.045

* The data format used is an exponential form, i.e., X.XX-Y is equivalent to X.XX 10^{-Y}.

† Mole fractions less than 10^{-4} are indicated by -.

Properly designed and operated incineration is therefore considered as the best present and near future method for the disposal of concentrated polychlorocyclodiene pesticide wastes.

Option No.2 - Chemical Degradation. The use of chemical reagents to decompose concentrated pesticide wastes to less toxic forms has been investigated by Kennedy et al and Sweeny and Fischer.[1782] The Mississippi State work showed that liquid ammonia and metallic sodium or lithium would completely decompose dieldrin, but the reagents are dangerous to use and the toxicity of the degradation products is not known. Sweeny and Fischer demonstrated that all five polychlorocyclodiene insecticides in this Profile Report could be substantially degraded by the mildly acidic reduction of zinc powder or zince-copper couple; however, the degradation products have not yet been identified and the soluble zinc ions formed are toxic and pose another environmental problem. Aldrin, dieldrin, endrin, and heptachlor are all resistant to the action of caustic alkalies, and chlordane is only partially degraded under the influence of caustic alkalies.[1618] Based on the results to date, chemical degradation could not be recommended as a method for the disposal of concentrated polychlorocyclodiene wastes.

Option No.3 - Sanitary Landfill. Soil burial of polychlorocyclodiene pesticide wastes, because of their extended persistance of up to six years, is not a satisfactory means of disposal. In the case of aldrin and heptachlor, their activity is extended through the formation of their respective metabolites, dieldrin and heptachlor epoxide. Both dieldrin and heptachlor epoxide are more chemically inert and persistent than the pesticides they derive from, and heptachlor epoxide is also more toxic than heptachlor to all organisms.[1618] Sanitary landfill should therefore be only considered for the disposal of small quantities of pesticide wastes, and only at approved sites that are acceptable from a geologic and ground water hydrology standpoint.[0620]

Option No.4 - Deep-well. Although all the polychlorocyclodiene insecticides are practically insoluble in water, their persistence and stability in water and the potential contamination of ground water make deep-well at best a questionable method for the disposal of these pesticides. Deep-well disposal of chlordane manufacturing wastes is currently practiced at Velsicol's Marshall, Illinois plant.[1735] The method is not recommended by the National Working Group on Pesticides,[0620] and should be considered only under special situations where hazards would be nonexistent.

The disposal of polychlorocyclodiene pesticide wastes in open pits, lagoons, unapproved landfill sites , and by on-site burning or deep sea burial are not recommended practices because of the obvious contributions to air and water pollution.

To summarize, the adequate methods for treating dilute polychlorocyclodiene pesticide wastes are: (1) adsorption with powdered activated carbon; (2) adsorption with granular activated-carbon beds; (3) potassim permanganate addition for removing aldrin or heptachlor; (4) ozonation for removing aldrin; and (5) anaerobic degradation for removing aldrin, endrin, or heptachlor. The only adequate method for the disposal of concentrated polychlorocyclodiene pesticide wastes is incineration.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The future of the polychlorocyclodiene insecticide market is relatively unclear at the present moment. However, there is sufficient quantities of degraded and surplus material (due mainly to restrictions placed upon its utilization) to warrant that these pesticides be considered as candidate waste stream constituents for national disposal. Treatment facilities used to dispose of other types of pesticide wastes at National Disposal Sites are generally also adequate to handle the polychlorocyclodiene insecticides. For the treatment of dilute polychlorocyclodiene pesticide wastes, the recommended processes are:

Process	Order of Preference	Remarks
Activated-carbon bed	First Choice	Demonstrated technology; recommended unit operation at National Disposal Sites.
Potassium permanganate addition	Second Choice	Only applicable for removing aldrin and heptachlor.

The only process recommended for treating concentrated polychlorocyclodiene pesticide wastes at National Disposal Sites is incineration.

It should be noted that both the activated-carbon bed process and incineration could also be employed in the treatment of other types of polychlorocyclodiene pesticide wastes, such as alodan and isodrin wastes.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

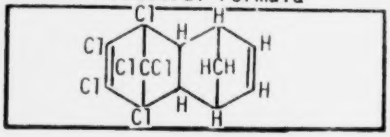
H.M.

H. M. Name Aldrin (13)

IUC Name 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endoexo-5,8 dimethanonaphthalene

Common Names

Structural Formula



Molecular Wt. 364.92 Melting Pt. 104 C(1) Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

$6X10^{-6}$ mm @ 25 C(2) @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 20 X 10^{-3} mg/liter (3) Hot Water Ethanol 5 g/100 ml(1)

Others: Highly soluble in acetone, amyl acetate, benzene, dipentene, dichloroethane, xylene, toluene, and carbon tetrachloride. (1), (2)

Acid, Base Properties

Highly Reactive with

Compatible with Alkalies and water at room temperature.(2)

Shipped in 1 and 5 gallon cans, 45 gallon drums

ICC Classification Poison B Coast Guard Classification Poison B

Comments The technical product is a brown mass containing 82% of aldrin, 12-13% analogs and about 5% various other compounds.

References (1) 1617

(2) 1618

(3) 0442

H.M.

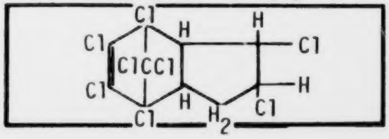
HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Chlorodane (484)

IUC Name 2,3,4,5,6,7,8,8-octachloro-4,7-endomethylene-2,3,3a,4,7,7a-hexahydroindene

Common Names Hexachlorodicyclopentadiene
Chloroindan

Structural Formula



Molecular Wt. 409.75 Melting Pt. 104-108 C (1) Boiling Pt. ______

Density (Condensed) 1.61 @ 25 C (1) Density (gas) ______ @ ______

Vapor Pressure (recommended 55 C and 20 C)

1×10^{-5} mm @ 25 C (1) 2 mm @ 175 C (Tech. product) @ ______ °

Flash Point ______ Autoignition Temp. ______

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water practically insoluble (2) Hot Water ______ Ethanol ______

Others: highly soluble in aromatic hydrocarbons and their halogen derivatives, ketones, esters, kerosene, ethers (1),(2)

Acid, Base Properties A small amount of HCl is given off when chlordane is acted on by water and moist chlordane strongly corrodes metals. (2)

Highly Reactive with ______

Compatible with ______

Shipped in 1- and 5-gallon cans, 45 gallon drums

ICC Classification ______ Coast Guard Classification ______

Comments Technical chlordane is a dark brown viscous liquid with cedar-like odor, but the product when refined is a pale yellow liquid. It is employed in the form of emulsions or solutions in organic solvents of petroleum origin. (2)

References (1) 1617
(2) 1618

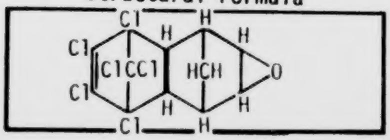
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Dieldrin (149)

IUC Name 1,2,3,4,10,10-hexachloro-t,7,-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-exo-5,8-dimethanonaphthalene

Common Names

Structural Formula



Molecular Wt. 382.93 Melting Pt. 175-176 C(2) Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

$1.8\ X10^{-7}$ mm @ 25 C(2) @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water $5X10^{-6}$% at 25 C(2) Hot Water Ethanol 4g/100 ml(1)

Others: Highly soluble in many organic solvents, but its solubility is considerably less than that of aldrin.

Acid, Base Properties

Highly Reactive with

Compatible with the action of alkalies(1)

Shipped in 25 gallon fiber drums (dry powder), 1 - and 5 - gallon cans and 45 gallon drums (solutions)

ICC Classification Poison B Coast Guard Classification

Comments The technical grade product is a light brown material with a solidification point above 95 C and contains about 85% dieldrin.(2)

References (1) 1617

(2) 1618

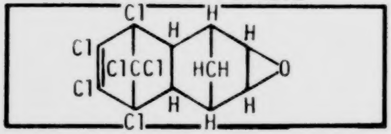
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Endrin (170)

IUC Name 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-,4-endo,endo-5,8-dimethanonaphthalene

Common Names

Structural Formula



Molecular Wt. 382.93 Melting Pt. 200 C (decomp.)(2) Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

$2X10^{-7}$mm @ 25 C @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.19 ppm(3) Hot Water Ethanol

Others: Highly soluble in most organic solvents.(2)

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in 25 gallon fiber drums (dry powder), 1-and 5-gallon cans, 45 gallon drums (solutions)

ICC Classification Poison B Coast Guard Classification

Comments The technical grade product is brown and contains not less than 85% of the principal compound

References (1) 1617
(2) 1618
(3) 0441

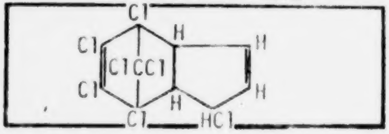
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Heptachlor (496)

IUC Name 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene

Common Names

Structural Formula



Molecular Wt. 372.28 Melting Pt. 95-96 C(2) Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

3×10^{-4} mm @ 25 C(1) @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water practically insoluble Hot Water Ethanol 4.5%(2)

Others: highly soluble in aromatic hydrocarbons, halogenated hydrocarbons, kerosene, acetone, carbon tetrachloride. (1),(2)

Acid, Base Properties

Highly Reactive with

Compatible with water and resistant to the action of caustic alkalies.(2)

Shipped in 25 gallon fiber drums (dry powder), 1-and5-gallon cans and 45 gallon drums (solutions)

ICC Classification Coast Guard Classification

Comments The pure compound is white crystalline material. The technical grade product is a waxy mass that contains 65-72% heptachlor and 28-35% related compounds.(2)

References (1) 1617
(2) 1618

PROFILE REPORTS ON
HIGHLY CHLORINATED HYDROCARBON PESTICIDES

Benzene Hexachloride (55), DDD (136), DDT (137)

1. GENERAL

Introduction

Both DDT and benzene hexachloride (BHC) were first synthesized in the last century but it was not until much later, around 1940, that their insecticidal properties were discovered.[1617] DDT has had unprecedented development as a synthetic insecticide since then because of its unusual combination of properties of broad spectrum insecticidal action, ease of manufacture, prolonged stability and residual activity[*], and relatively low mammalian toxicity. It was one of the first pesticides manufactured on a large scale and easily holds the record for total volume of any organic pesticide ever produced. Benzene hexachloride is known to have eight stereoisomers, but only one, the γ-isomer, is an active insecticide. The γ-isomer is also known as lindane and mixtures that contain 99 percent of the γ-isomer are known as lindane. The technical grade BHC product containing 10 to 50 percent γ-isomer is seldom used now. DDD (TDE) is one of the metabolites of DDT. It is somewhat less effective against most insects, but has the advantage of lower acute toxicity to warm-blooded animals and fish.

Although the growth of chlorinated hydrocarbon insecticides has been phenomenal in the past, in recent years they have not fared well because of the competition from new products which are better, cheaper, less toxic, and more readily degradable, and the trend is towards a decreasing share of the total pesticide market. The U.S. production figures for DDT, BHC, and lindane from the year 1960 to 1967 are[0449,1610]:

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[*] This is not necessarily considered as a desirable effect any more.

Annual Production (Thousand lb)

	1960	1961	1962	1963	1964	1965	1966	1967
DDT	164,180	171,438	167,032	178,913	140,783	140,783	141,349	103,411
BHC	37,444	25,080	12,022	6,778	6,000	----	6,000	----
Lindane	6,900	7,700	3,400	1,800	----	----	----	----

The production figures for BHC include those of its γ-isomer lindane. Individual production figures for DDD are not available, but based on the quantities used on crops,[0449] it is estimated that 12,400,000 lb of DDD were manufactured in 1964. These production figures illustrate the decline of both BHC and DDT-BHC has been gradually displaced by the dieldrin-heptachlor class of compounds that are more specific and effective, while the production of DDT has been fluctuating and is now well below its peak of the early 1960's. In 1970 only 59,316,000 lb of DDT were produced.[1718]

Manufacture

Benzene Hexachloride. BHC is normally made by the photochemical chlorination with ultraviolet light irradiation of the reaction medium.[1618] The chlorination is typically carried out in a reaction vessel fitted with a mercury lamp, at atmospheric pressure and a temperature of 20 to 60 C. The crude product after initial purification contains up to 24 percent γ-isomer, and lindane is obtained following further fractional crystallization. Today the only BHC producer in the United States is Hooker Chemical Corporation, Niagara Falls, New York.[0449,1690,1691]

DDT. The principal method of producing DDT is the condensation of chlorobenzene with chloral in the presence of a dehydrating agent such as concentrated sulfuric acid[1618]:

$$2\ \mathrm{ClC_6H_5} + \mathrm{C\ Cl_3CHO} \longrightarrow (\mathrm{ClC_6H_4})_2\ \mathrm{CHCCl_3} + \mathrm{H_2O}$$

There is, however, considerable variation in process equipment, design, reactant concentrations, and methods of purification in DDT manufacture. The only remaining U.S. producer of DDT is Montrose Chemical Company in Torrance, California.[1522]

DDD. DDD is produced by the condensation of chlorobenzene with dichloroacetaldehyde, which must be quite pure and not contain chloral as an impurity[1618]:

$$2\ ClC_6H_5 + CHCl_2CHO \longrightarrow (ClC_6H_4)_2\ CHCHCL_2 + H_2O$$

Both Rohm and Haas and Allied Chemical have discontinued their DDD manufacturing operations. DDD is not currently produced in the United States.[1695]

Uses

BHC was used extensively in the control of grasshoppers, cotton insects, wireworms and other soil pests but its application is now in the process of being almost phased out completely. However, the pesticide containing 99 to 100 percent of the γ-isomer of BHC, known as lindane, is still utilized in combined formulations with other disinfectants for seed treatments and with DDT to control the Colorado potato beetle and other pests.

DDT has been employed for the control of hundreds of species of insect pests of orchard, garden, field, and forest, as a mosquito larvicide, as a residual spray in dwellings for malaria eradication, and as a dust applied to humans in mass delousing programs for typhus control.[1433] DDD, although usually a less effective insecticide than DDT, is superior for the control of such insects as mosquito larvae, tomato hornworms, and the red-banded leaf roller.[1433]

Sources and Types of Pesticide Wastes

The sources of pesticide wastes may include the following[0620] (1) Pesticide manufacturers; (2) pesticide formulators; (3) pesticide wholesalers; (4) professional applicators; (5) cooperage facilities that recondition drums; (6) agricultural users; (7) government facilities that store, transport, and use pesticides; (8) urban and suburban home and garden users; (9) commercial and industrial processes including those from rug and fabric treatment facilities manufacturing plants, hospitals, etc.

In general, pesticide wastes can be classified as either diluted or concentrated wastes. Diluted pesticide wastes include those generated in the waste waters of the manufacturers, formulators, agricultural runoffs, and possibly spent caustic solutions used to clean empty pesticide containers. Concentrated pesticide wastes include any unused or contaminated pesticides, pesticide materials left in containers after emptying, sludges formed in treating waste water containing pesticides, sawdust or straw used to soak up accidental pesticide spills.

Chlorinated hydrocarbon pesticides appear as waste stream constituents in varied forms and compositions. Typical waste streams containing DDT are as follows:

30 percent DDT; 10 percent trichloroethane and benzylchlorophenol; 60 percent mixed hydrocarbons

10 percent DDT; 11 to 18 percent DDT decomposition products; 5 percent benzensulfonic acid; 30 percent aqueous sulfuric acid

DDT (unknown amount); aqueous waste containing Na_2SO_4

More detailed information relating to the forms and quantities of waste chlorinated hydrocarbon pesticides is presented in the Volume titled Waste Forms and Quantities.

Physical and Chemical Properties

The physical and chemical properties of lindane, DDD, and DDT are included in the attached worksheets. The compound DDT can exist in 27 isomeric forms, depending on the position of the substituted chlorine form. The physical and chemical properties given in the attached worksheet are for that of the p,p'-isomer, 2,2-bis(p-chlorophenyl)-1,1, 1-trichlorobenzene which makes up about 70 percent of the technical grade of DDT, and is the most active insecticidal principal. The technical grade DDT has a much lower melting point of around 90 C and is composed of at least thirteen identifiable compounds (Table 1).

TABLE 1[0445]

APPROXIMATE COMPOSITION OF TECHNICAL DDT[0445]

Compound	Approximate Percentage
1,1,1-Trichloro-2,2-bis(p-chlorophenyl) ethane (p,p'-DDT)	63-77
1,1,1-Trichloro-2-(o-chlorophenyl-2-(p-chlorophenyl) ethane (o,p'-DDT)	8-21
1,1-Dichloro-2,2-bis(p-chlorophenyl) ethane (p,p'-TDE)	0.3-4.0
1,1-Dichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl) ethane (o,p'-TDE)	0.04
1-o-Chlorophenylethyl-2-trichloro-p-chlorobenzene sulfonate	0.1-1.9
2-Trichloro-1-p-chlorophenylethanol	0.2
Bis(p-chlorophenyl) sulfone	0.03-0.6
α-Chloro-α-p-chlorophenylacetamide	0.01
α-Chloro-α-o-chlorophenylacetamide	0.01
Chlorobenzene	0.3
p-Dichlorobenzene	0.1
1,1,1,2-Tetrachloro-2-(p-chlorophenyl) ethane	present
Sodium p-chlorobenzenesulfonate	0.02
Ammonium p-chlorobenzenesulfonate	0.01
Inorganic	0.01-0.1
Unidentified and losses	5.1-10.6

2. TOXICOLOGY

The insecticidal activity of DDT is related to the ease with which it is absorbed by the insect but despite years of intensive research, the critical biochemical lesion is unknown. DDT affects peripheral sensory organs to produce violent trains of afferent impulses that produce hyperactivity and then convulsion of the insect. The paralysis and death that ensue are thought to occur from metabolic exhaustion or from elaboration of a naturally occuring neurotoxin. The exact modes of action of both DDD and lindane on insects are not known, but it has been suggested that like DDT they may interact with the pores of the lipoprotein structure of the insect nerve, causinq distortion and consequent excitation of nerve impulse transmission.[0509]

DDT, DDD, and lindane are all of only moderate toxicity to higher animals. DDT and DDD are readily absorbed from the intestinal tract, and may be taken into the lung and readily absorbed when occuring in the air in the form of an aerosol or dust. DDT, DDD, or lindane in solution may also be absorbed through the skin.

Acute poisoning of DDT may result in tremors of the head and neck muscles, tonic and clonic convulsions, cardiac or respiratory failure, and death. The estimated oral fatal dose is 500 mg/kg body weight of the solid material, with death occuring in 2 to 24 hours. Effects of chronic poisoning may include hepatic damage, central nervous system degradation, agranulocytosis, dermatitis, weakness, convulsions, coma, and death.[1492]

DDD is less toxic to humans than DDT. Acute poisoning of DDD produces lethargy but no convulsions. The estimated fatal oral dose is 5g/kg body weight. Chronic poisoning leads to atrophy of the adrenal cortex and liver damage.[1492]

Acute poisoning of lindane may be indicated by dizziness, headache, nausea, vomiting, diarrhea, tremors, weakness, convulsions, dyspnea, cyanosis, and circultory collapse. The estimated oral fatal dose is

150 mg/kg body weight. Topical use may cause local sensitivity reactions, and vapors may irritate the eyes, nose, and throat. Some evidence suggests that chronic toxicity may cause hepatic damage.[1492]

The acute oral and dermal LD_{50} values of DDT, DDD, and lindane to rats have all been well established (Table 2). The acute oral LD_{50} value of DDT and lindane is of the order of 100 mg/kg body weight, but for that of the less toxic DDD is around 3400 mg/kg body weight.[1277] The American Conference of Governmental Industrial Hygienists 1971 recommended Threshold Limit Values (TLV) for the compounds in mg/M^3 of air are[0225]: DDT, 1.0; lindane, 0.5. No TLV for DDD is given, but because of its lower toxicity to humans, it is felt that the established TLV for DDT would also serve as an adequate criterion for DDD.

The 48-hour Median Tolerance Limits (TL_m) for DDT, DDD, and lindane for various types of fresh water organisms have been established by the Federal Water Pollution Control Administration (Table 3). These data are indicative of the water pollution hazards associated with the use of the three insecticides.

Of special concern recently are the stability and lipoid solubility of the highly chlorinated hydrocarbon insecticides, which cause them to accumulate in animal tissues and to be magnified in concentration through food chains. Although the presence of DDT, DDD, or lindane in animal, bird, or fish tissues has not been proven to produce any direct toxic effects, the residues do interfere with calcium deposition in eggs, thus causing thin-shelled eggs to be laid and leading to a loss in bird reproduction.[0449] Furthermore, it has been suggested that following changes in feeding conditions, fish may draw on their fat reserves which in turn may release into their metabolism concentrations of DDT, DDD, or lindane that may then prove to be lethal.[1611]

TABLE 2.

ACUTE ORAL AND DERMAL LD_{50} VALUES OF HIGHLY CHLORINATED HYDROCARBON INSECTICIDES FOR WHITE RATS[1277]

Insecticides	Oral LD_{50} (mg/kg)		Dermal LD_{50} (mg/kg)	
	Males	Females	Males	Females
DDT	113	118	-----	2510
DDD	(3400)		(4000-rabbits)	
Lindane	88	91	1000	900

TABLE 3.

48-HOUR TL_m VALUES FROM STATIC BIOASSAY (in micrograms per liter)[0536]

Insec-ticide	Stream Invertebrate Species	TL_m	Cladocerans Species	TL_m	Fish Species	TL_m	Gammarus Lacustris TL_m
DDT	P. Californica	19	D. pulex	0.36	Bass	2.1	2.1
DDD	P. Californica	1100	D. pulex	3.2	Rainbow t	9	1.8
Lindane	P. Californica	8	D. pulex	460	Rainbow t	18	88

3. OTHER HAZARDS

All three insecticides are relatively stable to the action of heat. When heated to decomposition, however, they emit highly toxic fumes of chlorine, hydrogen chloride, and possibly phosgene in the case of lindane.[0766]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Care should be exercised in handling DDT, DDD, or lindane because of their toxicity and the dangers of absorption through the skin. The use of rubber gloves, goggles, a respirator, and protective clothing is advisable in the handling and application of these insecticides, and any spilled on the skin should be removed as soon as possible with plenty of water and soap.

DDT, DDD, or lindane should all be stored in well ventilated areas, away from any foodstuffs, feeds, or any other material intended for consumption by humans or animals, and preferably in a separate building. Ample warning signs should be posted in storage areas.

No Department of Transportation shipping labels are required for DDT, DDD, and lindane, as the hazards in shipping these insecticides are generally considered as minimum.[0619]

The National Agricultural Chemicals Association has established a Pesticide Safety Team Network with Area Coordinators throughout the country to provide nationwide 24-hour service. The network became operational on March 9, 1970 (with a central telephone number [513]-916-4300) and should be consulted in all cases of accidents, spills, leakage, fires, and other types of disasters involving DDT, DDD or lindane.

Disposal/Reuse

Contaminated or degraded DDT, DDD, or lindane could not be practically considered for reprocessing. The safe disposal of these insecticides is defined in terms of provisional limits in the atmosphere and a potable water source and/or marine habitat. The provisional limits are as follows:

Contaminant in Air	Provisional Limits	Basis for Recommendation
DDT	0.01 mg/M^3	0.01 TLV
DDD	0.01 mg/M^3	0.01 TLV
Lindane	0.005 mg/M^3	0.01 TLV

Contaminant in Water and Soil	Provisional Limits	Basis for Recommendation
DDT	0.05 ppm (mg/l)	Stokinger and Woodward Method
DDD	0.05 ppm (mg/l)	Based on similar compounds
Lindane	0.025 ppm (mg/l)	Stokinger and Woodward Method

The point source control strategy of monitoring waste effluents is suggested as the best current solution of minimizing water pollution by DDT, DDD, and lindane.[1612] Analysis of a combination of stream water, mud, and aquatic life is considered as inadequate because of the persistence of these compounds, which makes it difficult to relate the presence of the pesticides to the time and place of their introduction. On the other hand, it should also be recognized that the highly chlorinated hydrocarbon pesticides do play a legitimate and valued role in our present society, and full control of water pollution by these pesticides is not now attainable, as runoffs will be a continuing source for some years to come.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Dilute Pesticide Wastes

Option No.1 - Adsorption with Powdered Activated Carbon.* The effectiveness of powdered activated carbon on the removal of DDT from water has been reported by Sigworth[1635] and Whitehouse,[0445] and the removal of lindane from water by Robeck et al[0441] and Sigworth.[1635] Sigworth's studies were conducted with initial concentrations of 5 ppm DDT and 25 ppm lindane, and he concluded that 10 ppm carbon dosages in a treatment plant would accomplish 90 percent removal of most of the pesticides that are extensively used today. Whitehouse investigated the effect of carbon dosage and contact time on DDT removal from water, with initial DDT concentration of 0.0044 ppm, and showed that over 90 percent DDT removal could be obtained after one hour and carbon dosages above 100 ppm. Robeck et al investigated initial lindane concentrations of 10 ppb and found that 90 percent of the lindane could be removed with powdered activated carbon dosage of 30 to 70 ppm. The necessary dosage and the associated degree of removal of DDD should be in the same range as those for DDT. From the results of these studies, it is seen that the addition of powdered activated carbon to a liquid solution followed by stirring and filtration is an adequate and acceptable technique for treating dilute DDT, DDD, or lindane wastes.

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* The contaminated carbon could be regenerated in a multi-hearth furnace under a controlled atmosphere at temperatures in excess of 1600 F, so that the adsorbed impurities are voltalized and selectively oxidized from the surface of the carbon.

Option No.2 - Adsorption with Granular Activated-Carbon Beds.* The effectiveness of granular activated beds to remove DDT and lindane from water has been investigated by Robeck et al.[0441] Following passage through two carbon columns, it was found that initial concentrations 0.1 ppb DDT and 7.7 ppb lindane in water were reduced to below 0.01 ppb. Treatment of waste water containing a variety of pesticide wastes with granular activated-carbon bed has been practiced by Fisons Pest Control Ltd., in England since 1955,[1035,1631] where 99 percent removal of the pesticides are obtained. The treated effluent is diluted with river water before discharge to the river, and the results of government biological surveys indicated no effects of the discharge on the river. Because of the adequate contact time provided and the fact that it is a well established chemical engineering unit operation, adsorption with granular activated-carbon beds should be considered as one of the most satisfactory methods for treating dilute DDT, DDD, or lindane wastes.

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* The contaminated carbon could be regenerated in a multi-hearth furnace under a controlled atmosphere at temperatures in excess of 1,600 F, so that the adsorbed impurities are voltalized and selectively oxidized from the surface of the carbon

Option No.3-Coagulation and Filtration. As early as 1945 Carollo[1634] showed that coagulation, sedimentation, and filtration could be used to remove from 80 to 90 percent of the DDT in a water supply originally containing 0.1 to 10 ppm suspended DDT. The treatment apparently did not remove DDT in solution or extremely fine suspension, but complete removal (to less than 0.001 ppm) was effected when intimate contact with 1.65 to 15.0 ppm activated carbon was provided for fifteen minutes after coagulation and sedimentation and before filtration. The coagulants used in Carollo's study include alum, ferric chloride, and ferric sulfate, and the effectiveness of the method was demonstrated by the zero percent kill of A. aegypti (mosquito larvae) in treated water in 48 hours. In 1964 Robeck et al[0441] reported that 97 percent removal of 10 to 25 ppb DDT could be achieved by the conventional treatment with coagulation followed by sand filtration, whereas lindane was not removed. The recent study of Whitehouse,[0445] however, indicated that chemical coagulation alone was not effective in removing organic pesticides from water. Chemical coagulation followed by sand filtration or sedimentation-activated-carbon adsorption-filtration is therefore an adequate method for removing DDT or DDD (which is similar in chemical structure to DDT) from water, but not for lindane.

Option No.4-Alkaline Hydrolysis. Lindane has been reported by Metcalf[1617] and Melnikov[1618] to undergo dehydrochlorination in an alkaline environment to produce primarily 1,2,4-trichloroethane. Leigh [1629] observed that more than 98.5 percent of the lindane was removed at a pH of 11.5 in 6.5 hr. Metcalf[1617] and Melnikov[1618] also reported that DDT is dehydrochlorinated readily in alkaline solution with the formation of an insecticidally inert compound, whereas Leigh[1629] found that complete removal of DDT could be obtained at a pH of 11.1 in less than 24 hr. DDD is similarly dehydrochlorinated in alkali to form 2,2-bis-(p-chlorophenyl)-1-chloroethylene, although at a slower rate than DDT-the hydrolysis rate constants of DDT and DDD at 20 C being 0.0248 liter/sec/mole and 0.00567 liter/sec/mole respectively.[1617] From this information, it is apparent that alkaline hydrolysis in a properly designed mixing tank with sufficient residence time is an adequate process for treating dilute DDT, DDD, or lindane wastes.

Option No.5-Anaerobic Degradation. The anaerobic degradation of DDT,DDD and lindane has been investigated by Hill and McCarty.[1628] They concluded that under suitable, biologically active, anaerobic conditions the degradation of DDT, DDD, or lindane was far more rapid than under corresponding aerobic conditions. Anaerobic degradation in thick sludge at 95 F lowered the lindane concentration from 10 ppm to 5 ppm in 1 day, and to 0.5 ppm in 2 days. Under the same conditions DDT was converted almost immediately to DDD; the DDD was then degraded gradually but steadily and had a half-life of less than one week. Hill and McCarty also observed that the degradation of lindane and DDD appeared to follow first-order kinetics, and based on this assumption, the anaerobic degradation rate constants for lindane and DDD are 0.7/day and 0.1/day respectively at 95 F. It was also shown that temperature changes from 67 F to 95 F produced no significant effects on the degradation rates of DDT and DDD, although lindane degraded much more rapidly at the higher temperature.

Option No.6-Removal by Surface Active Agents. The removal of pesticides from water by the use of surface active agents to produce a foam has been investigated by Whitehouse.[0445] Although DDT, DDD, or lindane were not included in the study, the results with aldrin and dieldrin showed that up to 90 percent removal was attainable and demonstrated the value of the process as a possible near future treatment method for other types of pesticides.

The other treatment processes for the removal of DDT, DDD, or lindane from water that have been investigated include adsorption with clay, chemical oxidation, and aeration. Whitehouse[0445] showed that the removal of DDT and BHC by adsorption with clay was not totally satisfactory and only of the order of 20 to 25 percent. Buescher et al[0442] examined the effects of various chemical oxidants on lindane, and concluded that calcium hypochlorite, hydrogen peroxide, and sodium peroxide had no measurable effect on lindane, whereas potassium permanganate and ozone could remove only part of the lindane present. Robeck et al in 1965[0441] found that chlorine and potassium permanganate at 1 to 5 ppm did not reduce DDT or lindane, and that at relatively large and impractical concentrations, ozone did reduce DDT or lindane somewhat, but the by-products formed and their toxicity were unknown. The more recent study by Leigh in 1969[1629] confirmed the earlier findings, and showed that none of the oxidants used--potassium permanganate, potassium persulfate, or chlorine--were significantly effective in removing lindane or DDT from water. The removal of DDT and BHC from water by aeration was found to be a significant factor by Whitehouse,[0445] but again removal was only partial. These processes are therefore considered as inadequate methods for treating dilute DDT, DDD, or lindane wastes.

Concentrated Pesticide Wastes

Option No.1 - Incineration. The complete and controlled high temperature oxidation of DDT, DDD, or lindane in air or oxygen with adequate scrubbing and ash disposal facilities offers the greatest immediate potential for the safe disposal of these pesticides. The research on incineration of pesticides conducted by Kennedy et al at Mississippi State University had led to the conclusion that temperatures at or near 1,800 F will be sufficient to degrade 100 percent of DDT and 99 percent or more of most reagent-grade pesticides and commercial pesticide formulations.[0062,0063] It is expected that either a rotary kiln or liquid combustor, depending upon the form of the waste, followed by secondary combustion and aqueous caustic scrubbing would be an acceptable disposal method. Primary combustion should be carried out at a minimum of 1,500 F for at least 0.5 seconds with secondary combustion at a minimum temperature of 2,200 F for at least 1.0 second. In the case of DDT, the volatile products identified from burning of the formulation at 1,650 F include carbon monoxide, carbon dioxide, chlorine and hydrogen chloride. The equilibrium product distributions resulting from the thermal decomposition and combustion of DDT at Atmospheric pressure and three temperatures, 2,190 F (1,200 C), 1,470 F (800 C), 930 F (500 C), have also been computed using the TRW Chemical Analysis Program (Table 4). The results again indicate the possible formation of hydrogen chloride, but that at higher air/fuel ratios, complete combustion is obtained and neither methane nor carbon monoxide are found. As the same combustion products will be obtained in the incineration of DDD or lindane, an adequate gas clean up system to remove chlorine and hydrogen chloride must be installed to alleviate the air pollution problem. The abatement

TABLE 4.

EQUILIBRIUM COMPOSITION OF DDT/AIR SYSTEM

Wt % Pesticide	Temp.	CH_4	CO	CO_2	H_2	H_2O	HCl	HCN	N_2	Condensed Phase Graphite Mol/100G Feed
100	1200 C	2.331-4	-	-	2.853-1	-	7.144-1	-	-	1.706
	800 C	3.617-3	-	-	2.795-1	-	7.169-1	-	-	1.696
	500 C	6.596-2	-	-	1.726-1	-	7.614-1	-	-	1.522
70	1200 C	1.000-4	1.205-1	-	1.867-1	-	4.678-1	2.673-4	2.246-1	0.840
	800 C	1.541-3	1.148-1	1.880-3	1.824-1	2.736-3	4.706-1	-	2.260-1	0.851
	500 C	2.372-2	1.143-2	3.275-2	1.035-1	5.733-2	5.210-1	-	2.502-1	1.039
50	1200 C	-	2.039-1	-	1.185-1	-	2.969-1	2.771-4	3.802-1	0.119
	800 C	6.191-4	1.924-1	5.280-3	1.156-1	2.907.3	2.995-1	-	3.837-1	0.147
	500 C	8.854-3	1.790-2	8.033-2	6.325-2	5.486-2	3.397-1	-	4.351-1	0.517
20	1200 C	-	-	1.040-1	-	5.514-2	1.236-1	-	6.656-1	-
	800 C	-	-	1.044-1	-	6.129-2	1.123-1	-	6.688-1	-
	500 C	-	-	1.055-1	-	8.321-2	7.096-2	-	6.757-1	-

The data format used is an exponential form, i.e., X.XX-Y is equivalent to X.XX 10^{-Y}

Mole fractions less than 10^{-4} are indicated by - .

problem may be simplified by insuring against elemental chlorine formation through injection of steam or methane into the combustion process. Incineration with scrubbing has also been used successfully in the disposal of highly chlorinated hydrocarbon wastes from the manufacture of chlorinated solvents.[1690] Properly designed and operated incineration is therefore considered as the best present and near future method for the disposal of concentrated DDT, DDD, or lindane wastes.

Option No.2 - Chemical Degradation. The use of chemical reagents to decompose concentrated pesticide wastes to less toxic forms has been investigated by Kennedy et al[0062,0063] and Sweeny and Fischer.[1782] The Mississippi State work showed that liquid ammonia and metallic sodium or lithium would completely decompose DDT, but the reagents are dangerous to use and the toxicity of the degradation products are not known. Sweeny and Fischer demonstrated that the degradation of DDT can be effected by a mildly acidic solution of zinc powder or zinc-copper couple. The principal degradation product is bis(p-chlorophenyl) ethane, or DDT with all three aliphatic chlorines removed; however, although this material has been stated to be void of the neurotoxic effects of DDT, it nevertheless processes insecticidal properties and thus detoxification of DDT is not complete. In the same study, Sweeny and Fischer also found that lindane could be completely degraded by the mildly acidic reduction of zinc powder, although the degradation products have not been identified. Caustic alkalies have been used to decontaminate DDT, DDD, or lindane containers, but their actions on the concentrated pesticide wastes at ambient temperatures are relatively slow and involve the evolution of noxious hydrogen chloride.[1618] Based on the results to date and the effectiveness of incineration by comparison, chemical degradation could not be recommended as a method for the disposal of concentrated DDT, DDD, or lindane wastes, especially when large quantities of these pesticide wastes are involved.

Option No.3 - Sanitary Landfill. Soil burial of DDT, DDD, or lindane wastes, because of their extended persistence of up to four years, is not a satisfactory means of disposal. The method should only be considered for the disposal of small quantities of pesticide wastes, and only at approved sanitary landfill sites that are acceptable from a geologic and ground water hydrology standpoint.[0620]

Option No.4 - Deep well. Although DDT, DDD, and lindane are all only sparingly soluble in water, their persistence and stability in water and the potential contamination of ground water make deep well at best a questionable method for the disposal of these pesticides. Deep well disposal of pesticide wastes is not recommended by the National Working Group on Pesticides,[0620] and the method should be considered only under very special situations where hazards would be nonexistent.

The disposalof DDT, DDD, or lindane wastes in open pits, lagoons, unapproved landfill sites, and by on-site burning or deep-sea burial are not recommended practices because of the obvious contributions to air and water pollution.

To summarize, the adequate methods for treating dilute DDT, DDD, or lindane wastes are: (1) adsorption with powdered activated carbon; (2) adsorption with granular activated-carbon beds, (3) coagulation and filtration for DDT, or DDD; (4) alkaline hydrolysis; and (5) anaerobic degradation. The only adequate method for the disposal of concentrated DDT, DDD, or lindane wastes is incineration.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Although the use of DDT, DDD, and lindane are rapidly declining, there are sufficient degraded and surplus quantities (due mainly to restrictions placed upon their application) in the DOD and civilian sectors to warrant that these materials be considered candidate waste stream constituents for national disposal. The treatment facilities used to dispose of other types of pesticide wastes at National Disposal Sites are generally also adequate to handle DDT, DDD, or lindane wastes. For the treatment of dilute DDT, DDD, or lindane wastes, the recommended processes are:

Process	Order of Preference	Remarks
Activated-Carbon Beds	First Choice	Demonstrated technology; recommended unit operation at National Disposal Sites.
Alkaline Hydrolysis	Second Choice	Demonstrated technology; also applicable to other types of pesticides that are readily hydrolzyed in alkaline medium.

The only process recommended for treating concentrated DDT, DDD, or lindane wastes at National Disposal Sites is incineration. Both chemical degradation with strong alkaline solution and sanitary landfill are not considered suitable for the disposal of large volumes of concentrated pesticide wastes.

It should be noted that the activated-carbon bed process could also be employed in the treatment of other types of dilute pesticide wastes of the DDT or BHC family. Alkaline hydrolysis, on the other hand, does not have the same general applicability. For example, DDT analogs such as hexachlorobenzene and methoxychlor both degraded very slowly in alkaline medium. To dispose of other types of concentrated highly chlorinated hydrocarbon wastes, incineration is again the only recommended process.

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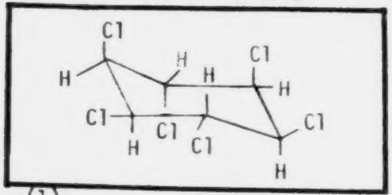
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Lindane (Benzene Hexachloride) (55)

IUC Name γ-1,2,3,4,5,6-Hexachlorocyclohexane

Common Names γ-isomer of BHC

Structural Formula



Molecular Wt. 290.84

Melting Pt. 112-113C(1)

Boiling Pt.

Density (Condensed) 1.85(1) @

Density (gas) @

Vapor Pressure (recommended 55 C and 20C)

9.4×10^{-6} mm @ 20 C (1)

@

@

Flash Point

Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.001 % (1)

Hot Water

Ethanol

Others: soluble in acetone, ethyl acetate, benzene, xylene(1)

Acid, Base Properties

Highly Reactive with

Compatible with actions of heat, light, and stable to oxidation(1)

Shipped in paper bags and fiber drums of various sizes

ICC Classification

Coast Guard Classification

Comments The pure γ-isomer is an almost odorless white crystalline material. It is formulated as solutions, aerosols, wettable powders, and emulsifiable concentrates.

References (1) 1617, p. 214-215.

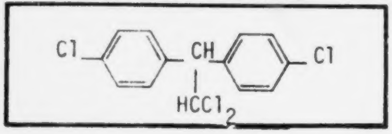
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name DDD (136)

IUC Name 2,2-bis-(p-chlorophenyl)-1, dichloroethane

Common Names TDE, dichlorodiphenyl dichloroethane

Structural Formula



Molecular Wt. 320.1   Melting Pt. 112C(1)   Boiling Pt. ______

Density (Condensed) ______ @ ______   Density (gas) ______ @ ______

Vapor Pressure (recommended 55 C and 20 C)

______ @ ______   ______ @ ______   ______ @ ______

Flash Point ______   Autoignition Temp. ______

Flammability Limits in Air (wt %)   Lower ______   Upper ______

Explosive Limits in Air (wt. %)   Lower ______   Upper ______

Solubility

Cold Water ______   Hot Water ______   Ethanol ______

Others: DDD has similar solubilities to DDT(1)

Acid, Base Properties ______

Highly Reactive with ______

Compatible with ______

Shipped in fiber drums, bags, tins, and bottles.

ICC Classification ______   Coast Guard Classification ______

Comments Crystalline solid. It is from 1/5 to 1/10 as toxic as DDT to mammals.(2)

References (1) 1618
(2) 1617

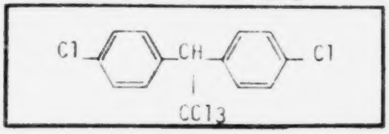
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name DDT (27 possible isomers)(137)

IUC Name 2,2-bis-(p-chlorophenyl)-1,1-trichloroethane

Common Names Dichlorodiphenyl trichloroethane, ethane
dicophane, chlorophenothane

Structural Formula



Molecular Wt. 354.5 Melting Pt. 108.5-109C Boiling Pt. ______

Density (Condensed) 1.6 @ ______ Density (gas) ______ @ ______

Vapor Pressure (recommended 55 C and 20 C)

1.9 X10^{-7}mm @ 20C(1) 1 mm @ 185 C(1) ______ @ ______

Flash Point ______ Autoignition Temp. ______

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water 0.001 mg/l(1) Hot Water ______ Ethanol ______

Others: soluble in ketones, esters of the lower fatty acids, aromatic hydrocarbons, and halogen derivatives of hydrocarbons(1)

Acid, Base Properties ______

Highly Reactive with ______

Compatible with actions of heat. Pure DDT does not decompose below 195 C, but the technical material decomposes at about 100 C(2)

Shipped in fiber drums, bags, tins, and bottles.

ICC Classification ______ Coast Guard Classification ______

Comments Colorless crystals or white to slightly off white powder. Technical DDT contains approximately 70 percent of p,p'-DDT which is the most effective insecticide principal. In application, DDT is formulated as dusts, concentrated emulsions, wettable powders, preparation for fine-droplet spraying, and aerosols.

References (1) 1618
(2) 1617

PROFILE REPORT

2,4-D (135)

1. GENERAL

Introduction

The discovery of the growth regulating properties of the chlorinated phenoxyacetic acids in 1944 and their subsequent employment as herbicides began the modern era of selective chemical weed control. These compounds are selective to broad-leaved weeds in cereals and could be absorbed from soil as pre-emergent herbicides. The growth regulating action is shared by a group of hundreds of related molecules all derived from the same parent substance, 2,4-dichlorophenoxyacetic acid or 2,4-D. In fact, to permit the proper application and formulation of 2,4-D, the amine salts and esters of the acid have been generally used instead of 2,4-D as such.

The chlorophenoxy groups of herbicides which includes 2,4-D, 2,4,5-T (2,4,5-trichlorophenoxy acetic acid) and MCPA (2-methyl-4-chlorophenoxy acetic acid) comprise approximately half the total domestic herbicide market. The U. S. production figures for 2,4-D from the year 1960 to 1967 in thousands of pounds are:[0449,1610]

Annual U. S. Production (thousand lb)

1960	1961	1962	1963	1964	1965	1966	1967
361,815	43,392	42,977	46,312	53,714	63,320	68,182	77,139

However, in 1970 only 43,576,000 lb of 2,4-D were produced.[1718] The production figures thus illustrate the gradual declining importance of 2,4-D as a base material for herbicides.

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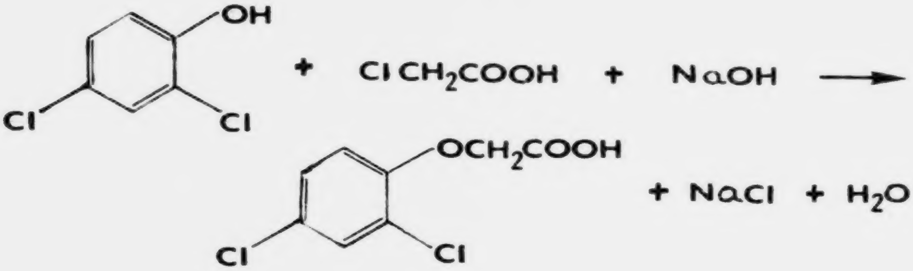
Manufacture

2,4-D is generally prepared by the condensation reaction of monochloroacetic acid and 2,4-dichlorophenol in an alkaline solution at atmospheric pressure, 60 to 80 C, and a residence time of 6 to 8 hr in a jacketed stirred reactor:[1610]



Large scale commercial facilities for the manufacture of technical grade 2,4-D in the United States include the following[1774, 1775, 1776, 1777, 1778, 1779, 1780]:

Dow Chemical Company, Midland, Michigan
Rhodia Inc., Chipman Division, Portland, Oregon
Transvaal Inc., Jacksonville, Arkansas

The Transvaal plant was formerly operated by Hercules Inc.

Uses

The chlorophenoxy acids are active by contact and by translocation from leaves to roots of perennial weeds and are used as pre-emergent applications to the soil for control of young seedlings. They are also effective for aquatic weed control, for the elimination of unwanted vegetation, and are selective against many broad-leaved annual weeds in cereal and grass crops.[0509]

In addition, 2,4-D and its derivatives have also found important uses in related fields such as thinning of fruit, prevention of preharvest drop, fruit setting, promotion of rooting and postharvest decay prevention.[0509]

Sources and Types of Pesticide Wastes

The sources of pesticide wastes may include the following:[0620] (1) pesticide manufacturers; (2) pesticide formulators; (3) pesticide wholesalers; (4) professional applicators; (5) cooperage facilities that recondition drum; (6) agricultural users; (7) government facilities that store, transport, and use pesticides; (8) urban and suburban home and garden users; (9) commercial and industrial processes including those from rug and fabric treatment facilities manufacturing plants, hospitals, etc.

In general, pesticide wastes can be classified as either diluted or concentrated wastes. Diluted pesticide wastes include those generated in the waste waters of the manufacturers, formulators, agricultural runoffs, and possibly spent caustic solutions used to clean empty pesticide containers. Concentrated pesticide wastes include any unused or contaminated pesticides, pesticide materials left in containers after emptying, sludges formed in treating waste water containing pesticides, sawdust or straw used to soak up accidental pesticide spills.

Unlike most pesticides, 2,4-D is also used as an aquatic herbicide and applied directly to lakes, rivers, irrigation waterways, and other surface waters for weed control, thus posing a potential water pollution problem. 2,4-D has been reported to persist for several months in lake waters.[1757]

Chlorophenoxy pesticides appear as waste stream constituents in varied forms and compositions. Typical waste streams containing chlorophenoxy compounds are as follows:

Solvents including toluene and xylene containing 1 to 5 percent 2,4-D and/or 2,4,5-T

Organic waste containing 20 to 25 percent 2,4-D; 20 to 25 percent 2,6-D; 10 to 15 percent mono- and trichlorophenoxy acetic acids

Still bottoms containing 2,4-D, 2,6-D and chlorophenols.

Solid wastes containing 0.5 percent 2,4-D

More detailed information relating to the forms and quantities of waste chlorophenoxy compounds is presented in the volume titled Waste Forms and Quantities.

Physical and Chemical Properties

The physical and chemical properties of 2,4-D are summarized in the attached worksheet.

2. TOXICOLOGY

2,4-D is of moderate acute toxicity to mammals. The acute oral and dermal LD_{50} values to the rat have been reported to be 375 and 1500 mg/kg body weight respectively.[1277] Inhalation of 2,4-D dusts and sprays is relatively harmless, and percutaneous absorption is negligible.[0449]

Chronically 2,4-D is of low toxicity, and can be ingested by animals and man in daily dosages approaching those which produce acute toxic effects when given only once. Thus, the cumulative effects of 2,4-D are minimal.

The American Conference of Governmental Industrial Hygienists 1971 recommended Threshold Limit Value (TLV) for 2,4-D in air is 10 mg/M^3.[0225]

The 48-hour Median Tolerance Limit (TL_m) for 2,4-D established by the Federal Water Pollution Control Administration for various types of fresh water organisms in micrograms per liter are:[0536] P. Californica (stream invertebrate), 1,800; Daphnia pulex (cladocerans), 3,200; Rainbow trout (fish), 960; and Gammarus lacustris, 1,800. These data are indicative of the hazards to aquatic life associated with the use of 2,4-D.

3. OTHER HAZARDS

As an organic acid, 2,4-D is corrosive and reacts with metals and bases. When heated to decomposition, highly toxic fumes of hydrogen chloride and other chlorinated products are emitted.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Although 2,4-D is only mildly toxic to humans, the use of rubber gloves, goggles, and a respirator is recommended in its handling and application. Storage of 2,4-D should be in a cool, dry, well-ventilated area, away from acute fire hazards, and with proper warning signs posted. No Department of Transportation shipping labels are required for 2,4-D, as the hazards in shipping 2,4-D are generally considered as minimum.[0278]

The National Agricultural Chemicals Association has established a Pesticide Safety Team Network with Area Coordinators throughout the country to provide nationwide 24-hour service. The network became operational on March 9, 1970 (with a central telephone number - [513] 916-4300) and should be consulted in all cases of accidents, spills, leakage, fires, and other types of disasters involving 2,4-D.

Disposal/Reuse

Contaminated or degraded 2,4-D could not be practically considered for reprocessing. The safe disposal of 2,4-D is defined in terms of the recommended provisional limits in the atmosphere and potable water source and/or marine habitat. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
2,4-D	0.1 mg/M^3	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
2,4-D	0.5 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Dilute Pesticide Wastes

Option No. 1 - Adsorption with Powdered Activated Carbon.* The effectiveness of powdered activated carbon on the removal of 2,4-D from water has been examined by Aly and Faust,[1789] Sigworth,[1635] and Whitehouse.[0445] Aly and Faust constructed adsorption isotherms for 2,4-D in accordance with the Freundlich equation, from which the amount of activated carbon required to reduce the 2,4-D concentration in water from 10 ppm to 1 ppm and 0.1 ppm was calculated to be 85 mg/liter and 318 mg/liter respectively. Sigworth's studies were conducted with initial 2,4-D concentrations of 1 and 6 ppm; however, the results obtained were inconclusive because of the possibility of employing inaccurate analytical procedures. Whitehouse investigated the effects of pH, contact time, and carbon dosage on 2,4-D removal from water, and showed that with an initial 2,4-D concentration of 100 ppm over 90 percent removal of 2,4-D could be achieved at pH values lower than 3.2 after one hour of mixing and a carbon dosage of 300 mg/liter. With a lower 2,4-D initial concentration of 10 ppm, a pH of 6, and one hour contact time, 90 percent 2,4-D removal could be obtained with a carbon dosage of 120 mg/liter and 99 percent 2,4-D removal with a carbon dosage of 320 mg/liter. Based on the results of the studies of Faust and Aly and Whitehouse, the addition of powdered activated carbon to a liquid solution (preferably at a lower pH) followed by stirring and filtration is an adequate method for treating dilute 2,4-D wastes.

Option No. 2 - Adsorption with Granular Activated-Carbon Beds.* Although the effectiveness of granular activated-carbon beds to remove 2,4-D from water has not been discussed in the literature per se, Robeck et al reported that following passage through the carbon columns, the concentration of 2,4,5-T (which is simply 2,4-D with an additional aromated chlorine) in water was reduced from 3.6 ppb to 0.05 ppb.[0441] Treatment of waste water containing a variety of pesticide wastes with granular activated-carbon beds have been practiced by Fisons Pest Control Ltd. in England since 1955, where over 99 percent removal of the pesticides are obtained.[1035, 1631] The treated effluent is diluted with river water before discharge to the river, and the results of government biological surveys indicated no effects of the discharge on the river. In the United States, both Rhodia and Dow utilized granular activated-carbon beds in the treatment of their 2,4-D manufacture waste water.[1777,1778] Activated-carbon bed adsorption was also originally employed as the treatment procedure for the waste water from 2,4-D manufacture at the Naugatuck Chemicals plant, Elmira, Ontario, Canada,[1630] although the method was later abandoned due to the high treatment cost associated with the removal of dichlorophenol at that time (1951). Because of the adequate contact time provided and the fact that it is a well established chemical engineering unit operation, adsorption with granular activated-carbon beds should be considered as one of the most satisfactory methods for treating dilute 2,4-D wastes.

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*The contaminated carbon could be regenerated in a multi-hearth furnace under a controlled atmosphere at temperatures in excess of 1600 F, so that the adsorbed impurities are voltalized and selectively oxidized from the surface of the carbon.

Option No. 3 - Biological Degradation. The biological treatment of 2,4-D waste water has been investigated by Mills[1630] and Sidwell.[1781] Mills reported that 2,4-D acid could be oxidized by bacterial action in the laboratory, but his pilot plant work with trickling filter and activated sludge systems were mainly concerned with the removal of dichlorophenol from the 2,4-D manufacture waste water, and no data on the removal of 2,4-D were given. Sidwell described the Jacksonville, Arkansas project on joint treatment of municipal waste water and 2,4-D manufacture waste water from the Transvaal Inc. plant. Pretreatment of the industrial effluent included processing through a crushed limestone filled neutralization ditch and an in-plant equilization pond, and a final pH adjustment to 7.2 by automatic addition of slaked lime slurry in a continuous stirred pit. The combined municipal-industrial waste water containing 2 to 4.2 mg/liter phenoxy acids was then treated in an aerated lagoon and stabilization pond system before discharge to the receiving stream. Although the removal of chlorophenoxy acids by the lagoon and pond system ranged from only 49 to 80 percent, the stabilization pond effluent with typically 1.1 mg/liter chlorophenoxy acids was considered to be good quality, as substantiated by the results of the biological surveys of the upper receiving stream conducted in December 1969 and December 1970. The continuous successful operation of the aerated lagoon - stabilization pond system at Jacksonville, Arkansas indicates that 2,4-D containing waste water when combined with sewage could be adequately treated by biological methods.

Option No. 4 - Ion Exchange. The use of ion exchange columns to remove the sodium salt of 2,4-D from water has been examined by Aly and Faust.[1636] The results of their studies showed that the sodium salt of 2,4-D when present in relatively high concentrations (120 mg/liter) could be completely removed from water by strongly basic anion exchange resins, and indicated that neutralization of 2,4-D to its sodium salt followed by passage through ion-exchange columns is an adequate method for treating dilute 2,4-D wastes.

Option No. 5 - Removal by Surface Active Agents. The removal of pesticides from water by the use of surface active agents to produce a foam has been investigated by Whitehouse.[0445] Although 2,4-D was not included in the study, the results with aldrin and dieldrin showed that up to 90 percent removal was attainable and demonstrated the value of the process as a possible near future treatment method for other types of pesticides.

The other treatment methods for the removal of 2,4-D from water that have been investigated include adsorption with clay, chemical coagulation, and chemical oxidation. The works of Faust and Aly,[0446] Schwartz[1756] and Whitehouse[0445] all suggested that adsorption with clay was an unsatisfactory method for removing 2,4-D from water. Faust and Aly[0446,1636] examined the effects of chemical oxidants on 2,4-D compounds and concluded that both chlorine and potassium permanganate were ineffective in the removal of 2,4-D compounds from water. The laboratory studies of Faust and Aly[0446] also showed that chemical coagulation with alum and ferric sulfate doses up to 100 ppm were ineffective in removing 2,4-D. These processes are therefore considered as inadequate methods for treating dilute 2,4-D wastes.

Concentrated Pesticide Wastes

Option No. 1 - Incineration. The complete and controlled high temperature oxidation of 2,4-D in air or oxygen with adequate scrubbing and ash disposal facilities offers the greatest immediate potential for the safe disposal of pesticides. The research on incineration of pesticides conducted by Kennedy et al at Mississippi State University has led to the conclusion that 2,4-D approached complete combustion at temperatures as low as 1,110 F and identified carbon monoxide, carbon dioxide, chlorine and hydrogen chloride as the volatile products from burning of the 2,4-D formulation at 1,650 F.[0062,0063] The equilibrium product distributions resulting from the thermal decomposition and combustion of 2,4-D at atmospheric pressure and three temperatures, 2,190 F (1,200 C), 1,470 F (800 C), 930 F (500 C) have also been computed using the TRW Chemical Analysis Program (Table 1). The results also indicate the possible formation of hydrogen chloride, but that at higher air/fuel ratios, complete combustion is approached and both methane and carbon monoxide are only present in small quantities. It is expected that either a rotary kiln or liquid combustor, depending upon the form of the waste, followed by secondary combustion and aqueous or caustic scrubbing would be an acceptable disposal method. Primary combustion should be carried out at a minimum of 1,500 F for at least 0.5 seconds with secondary combustion at a minimum temperature of 2,200 F for at least 1.0 second. The abatement problem may be simplified by insuring against elemental chlorine formation through injection of steam or methane into the combustion process. Incineration is also being considered by Rhodia, Inc., Portland, Oregon as a possible means of disposing the solid and semi-solid wastes generated in 2,4-D manufacture.[1777] In addition, combustion units designed for the disposal of chlorinated organic wastes and capable of recovering chlorine in the form of usable hydrogen chloride have been developed, and a 7,000 lb/hr plant is now under construction for E. I. du Pont de Nemours & Company in Victoria, Texas by Union Carbide Corporation.[1743] Properly designed and operated incineration is therefore considered as the best present and near future method for the disposal of concentrated 2,4-D wastes.

TABLE 1.

EQUILIBRIUM COMPOSITION OF 2, 4-D/AIR SYSTEM

(1 ATM PRESSURE) MOLE FRACTION, GAS PHASE*+

Wt % Pesticide	Temp.	CH_4	CO	CO_2	H_2	H_2O	HCl	HCN	N_2	Condensed Phase Graphite Mol/ 100 G Feed
100	1200 C	2.329-4	4.283-1	1.574-4	2.852-1	2.580-4	2.859-1	-	-	2.575
	800 C	3.522-3	3.883-1	2.151-2	2.758-1	1.400-2	2.967-1		-	2.667
	500 C	4.171-2	2.812-2	1.982-1	1.373-1	1.870-1	4.077-1	-	-	3.297
70	1200 C	1.002-4	4.010-1	1.380-4	1.870-1	1.585-4	1.875-1	2.671-4	2.238-1	1.472
	800 C	1.520-3	3.661-1	1.912-2	1.812-1	8.671-3	1.930-1	-	2.304-1	1.558
	500 C	1.832-2	2.772-2	1.925-1	9.099-2	1.222-1	2.499-1	-	2.983-1	2.213
50	1200 C	-	3.820-1	1.253-4	1.189-1	1.000-4	1.192-1	2.772-4	3.794-1	0.554
	800 C	6.167-4	3.508-1	1.756-2	1.154-1	5.292-3	1.220-1	-	3.883-1	0.633
	500 C	7.594-3	2.762-2	1.911-1	5.858-2	7.836-2	1.522-1	-	4.845-1	1.293
20	1200 C	-	7.792-2	1.560-1	8.168-3	4.322-2	5.198-2	-	6.621-1	-
	800 C	-	7.012-2	1.638-1	1.656-2	3.543-2	5.199-2	-	6.621-1	-
	500 C	1.045-3	2.771-2	1.924-1	2.173-2	2.916-2	5.300-2	-	6.750-1	0.056

*The data format used is an exponential form, i.e. X.XX-Y is equivalent to X.XX10^{-Y}

+Mole fractions less than 10^{-4} are indicated by -.

Option No. 2 - Chemical Degradation. The use of chemical reagents to decompose concentrated pesticide wastes to less toxic forms has also been investigated by Kennedy et al.[0062,0063] The Mississippi State work showed that liquid ammonia and metallic sodium or lithium would completely decompose 2,4-D, but the reagents are dangerous to use and the toxicity of the degradation products are not known. The action of caustic alkalies would only hydrolyze 2,4-D to the corresponding salts, and no further degradation could be obtained. Based on these results and the superiority of incineration by comparison, chemical degradation could not be recommended as a method for the disposal of concentrated 2,4-D wastes.

Option No. 3 - Application to Soil Surface. Research on the reduction of 2,4-D waste process liquors into biologically inactive compounds by means of application to and degradation in the soil surface has been conducted at Alkali Lake in eastern Oregon under the direction of R. L. Goulding of Oregon State University since late 1969.[1754,1755] The results of the study to date suggested subsurface injection of 2,4-D as a useful, economic approach to control airborne losses of the waste component, and indicated clearly the apparent degradation of 2,4-D by soil microorganisms when applied at the rate 250 lb/acre equivalent of 2,4-D. Data derived from samples taken from the actual test plots showed that the 2,4-D concentration in the soil layer subjected to subsurface injection has declined from an initial 135 ppm to 30 ppm after a 480-day period. The Oregon State work in progress thus provides strong support to the adequacy of the soil surface application as a disposal method for concentrated 2,4-D wastes.

Option No. 4 - Deep Well. Although 2,4-D is only sparingly soluble in water, its persistence and stability in water and the potential contamination of ground water make deep well at best a questionable method for the disposal of 2,4-D. Incidents of ground water contamination that persisted for over 3 years leading to the damage of lawns, shrubs and crops, as a result of the penetration of the 2,4-D waste water through permeable sediments after being discharged to rivers or lagoons have been reported.[0446] Deep well disposal of 2,4-D wastes is currently being practiced at Dow Chemical Company, Midland, Michigan,[1778] but the method is not recommended by the National Working Group on Pesticides,[0620] and should be considered only under very special situations where hazards would be nonexistent.

The disposal of 2,4-D wastes in open pits, lagoons, unapproved landfill sites, and by on site burning or deep sea burial are not recommended practices because of the obvious contributions to air and water pollution.

To summarize, the adequate methods for treating dilute 2,4-D wastes are: (1) adsorption with powdered activated carbon; (2) adsorption with granular activated-carbon beds; (3) biological degradation; and (4) ion exchange.

The adequate methods for the disposal of concentrated 2,4-D wastes are (1) incineration, and (2) soil surface application.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is anticipated that disposal systems to handle both dilute and concentrated 2,4-D will still be required at National Disposal Sites located near formulators, users, and especially agriculture centers in the near future. The dilute 2,4-D wastes that will require treatment include spent cleaning solutions for 2,4-D containers and any other 2,4-D contaminated waste water. The concentrated 2,4-D wastes that will require treatment include any surplus, contaminated, partially or fully degraded pesticides.

The processes recommended for the treatment of dilute 2,4-D wastes at National Disposal Sites are:

Process	Order of Preference	Remarks
Activated-Carbon Beds	First Choice	Demonstrated technology on commercial scale; also adequate for removal of the sodium salt and esters of 2,4-D and most other types of pesticides from waste water.
Ion Exchange	Second Choice	Demonstrated technology; requires neutralization to the sodium salt first and not adequate for the removal of the 2,4-D esters from water.
Biological Degradation	Third Choice	Demonstrated technology on commercial scale; requires dilution with municipal sewage before treatment in aerated lagoons and stabilization ponds.

The processes for the treatment of concentrated 2,4-D wastes at National Disposal Sites are:

Process	Order of Preference	Remarks
Incineration	First Choice	Demonstrated technology; applicable to the disposal of organic pesticide wastes; possibility of recovering chlorine in the form of usable hydrogen chloride.
Soil Surface Application	Second Choice	Demonstrated technology; also applicable to the disposal of other types of herbicides that are degradable by soil microorganisms.

It should be noted that the activated-carbon bed and biological degradation processes could also be employed in the treatment of other types of dilute aryloxalkylcarboxylic acid wastes, such as 2,4,5-T and MCPA wastes. To dispose of other types of concentrated arloxalkylcarboxylic acid wastes, because of the lack of supporting data on soil surface application, incineration is the only recommended process.

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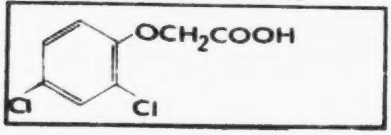
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name 2,4-D (135)

IUC Name 2,4-Dichlorophenoxyacetic acid

Common Names

Structural Formula



Molecular Wt. 221.05 Melting Pt. 138-140C(1) Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

0.4 mm @ 160C(2) @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.06% at 25C Hot Water Ethanol

Others: Highly soluble in ether, benzene, carbon tetrachloride, acetone, and tetra and pentachloroethanes (2)

Acid, Base Properties A typical organic acid that readily forms sodium, potassium, and ammonia salts.

Highly Reactive with

Compatible with

Shipped in fiber drums and bags.

ICC Classification Coast Guard Classification

Comments 2,4-D is a white crystalline substance when pure and has practically no odor; the technical grade compound, however, smells more or less like dichlorophenol.(2)

References (1) 0509
(2) 1618

PROFILE REPORTS ON
ORGANOPHOSPHORUS PESTICIDES

Methyl Parathion (274), Parathion (321), Demeton (491), Guthion (495)

1. GENERAL

Introduction

The practical development of organophosphorus insecticides is largely due to the original extensive work of G. Schrader beginning in 1937. Thousands of organophosphorus compounds of many types have been evaluated for insecticidal properties and the current commercially used compounds include insecticides that are marketed in multimillion pound quantities. The number of highly toxic organophosphorus compounds is virtually limitless and their suitability as insecticides depends on their physical and chemical properties and how safely they may be employed. Of the four organophosphorus insecticides included in this Profile Report: parathion and methyl parathion represent the two most widely used broad spectrum organophosphorus insecticides, demeton is one of the more successful plant systemic insecticides, and Guthion is one of the most toxic organophosphorus insecticides with prolonged activity.

Organophorphorus insecticides are among the fastest growing products in the pesticide industry. The U.S. production figures for parathion and methyl parathion from the year 1960 to 1967 are:[0449,1610]

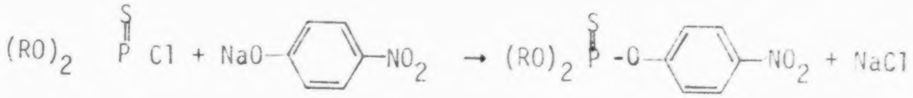
Annual Production (Thousand lb)

	1960	1961	1962	1963	1964	1965	1966	1967
Parathion	7,434	8,423	8,786	----	12,768	16,607	19,444	11,361
Methyl Parathion	11,794	18,527	16,156	15,999	18,640	29,111	35,862	33,344

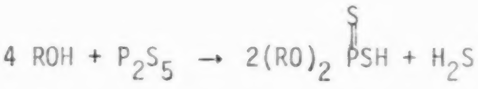
Individual production figures for Guthion and demeton are not available, but based on the quantities used on crops,[0449] it is estimated that 4,142,000 lb of Guthion and 377,000 lb of demeton were manufactured in 1964. The four organophosphorus insecticides investigated in this Profile Report accounted for approximately 60 percent of the total organophosphorus insecticide production in 1964.[0449]

Manufacture

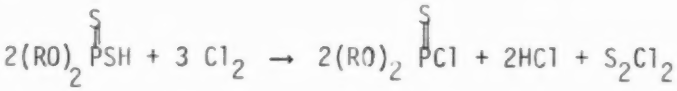
Parathion and Methyl Parathion. Both insecticides are manufactured from sodium p-nitrophenolate; parathion by reacting 0,0-dietnyl phosphorothiochloridate with the sodium compound, and methyl parathion from the reaction of the equivalent 0,0-dimethyl compound [1618]:



This process is usually carried out in aqueous medium or in organic solvents (chlorobenzene, xylene, aliphatic ketones). The phosphorothiochloridates necessary for the synthesis of the parathions are prepared by reacting the appropriate alcohol with phosphorus pentasulfide, followed by chlorination [1618]:



$$4\ ROH + P_2S_5 \rightarrow 2(RO)_2\overset{\overset{S}{\|}}{P}SH + H_2S$$

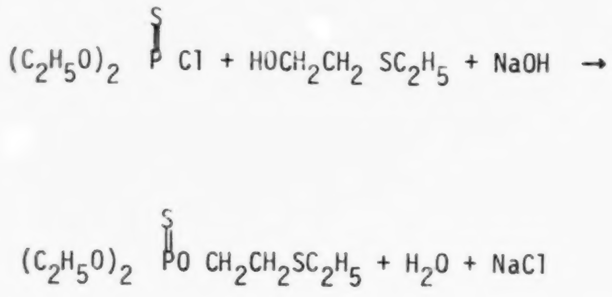


$$2(RO)_2\overset{\overset{S}{\|}}{P}SH + 3\ Cl_2 \rightarrow 2(RO)_2\overset{\overset{S}{\|}}{P}Cl + 2HCl + S_2Cl_2$$

Large scale commercial facilities for the manufacture of parathion and methyl parathion in the United States include the following [1592, 1531]:

Kerr-McGee Chemical Corporation, Hamiltion, Mississippi
Kerr-McGee Chemical Corporation, Los Angeles, California
Monsanto Chemical Company, Anniston, Alabama
Stauffer Chemical Company, Mount Pleasant, Tennessee

__Demeton.__ Demeton is produced by the reaction of 0,0-diethyl phosphorothiochloridate with 2-hydroxydiethyl sulfide in the presence of sodium hydroixde or carbonate of the alkali metals[1618]:

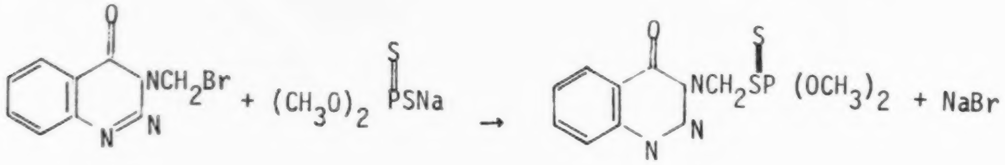


$$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}Cl + HOCH_2CH_2SC_2H_5 + NaOH \rightarrow$$

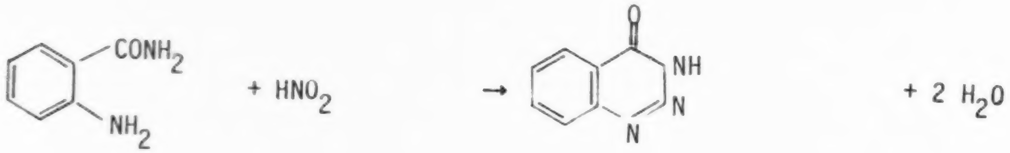
$$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}O\,CH_2CH_2SC_2H_5 + H_2O + NaCl$$

Demeton contains approximately two parts of the thiono-isomer and one part of the thiol-isomer, and the thiono-isomer compound obtained is partially isomerized directly in the process of preparation.

__Guthion.__ Guthion is produced by the reaction of the N-halomethyl derivatives of azimidobenzoyl with salts of dimethyldithiosphosphoric acid[1618]:



When the methylbromo derivative is used, Guthion is obtained in almost quantitative yield. The 4-oxo-3,4-dihydro-1,2-,3-benzotriazine necessary for the synthesis can be prepared from the amide of anthranilic acid by the action of sodium nitrite in acid medium[1618]:



Both demeton and Guthion are manufactured by Chemagro Corporation at their Kansas City, Missouri facility.

Uses

The principal application areas of the four organophosphorus insecticides have been summarized by Van Wazer[1620] (Table 1).

Sources and Types of Pesticide Wastes

The sources of pesticide wastes may include the following[0620]:

(1) Pesticide manufactures; (2) pesticide formulators; (3) pesticide wholesalers; (4) professional applicators; (5) cooperage facilities that recondition drums; (6) agricultural users; (7) government facilities that store, transport, and use pesticides; (8) urban and suburban home and home garden users; (9) commercial and industrial processes including those from rug and fabric treatment facilities manufacturing plants, hospitals, etc.

In general, pesticide wastes can be classified as either diluted or concentrated wastes. Diluted pesticide wastes include those generated in the waste waters of the manufacturers, formulators, agricultural runoffs, and possibly spent caustic solutions used to clean empty pesticide containers. Concentrated pesticide wastes include any unused or contaminated pesticides, pesticide materials left in containers after emptying, sludges formed in treating waste water containing pesticides, sawdust or straw used to soak up accidental pesticide spills.

Organophosphorus pesticides appear as waste stream constituents in varied forms and concentrations. Typical waste streams containing organophosphorus pesticides are as follows:

> Aqueous slurries containing 10 percent mixed Malathion
> and Parathion; 5 to 7 percent mixed intermediates;
> 3 to 4 percent carbaryls; 5 to 10 percent diatomoceous
> earth; 3 to 5 percent organic solvents

TABLE 1 [1620]

APPLICATION AREAS OF ORGANOPHOSPHORUS INSECTICIDES

	Crops											
Insecticides	Cotton	Fruit, Citrus	Fruits, Deciduous & Nuts	Grasses & Forage	Orna-ments	Potatoes	Small Grains	Sugar Cane & Beets	Soy Beans	Stored Crops	Tobacco	Vegetables
Guthion	X		X									X
Methyl Parathion	X						X					X
Paratnion	X	X	X	X	X	X	X	X	X	X		X
Demeton	X		X	X	X	X						

Solid wastes containing 0.5 percent parathions

Process solution containing 10 percent demeton and Guthion.

Solid wastes containing 0.5 percent demeton and Guthion.

More detailed information relating to the forms and quantities of waste organophosphorus pesticides is presented in the Appendix Volume titled Waste Forms and Quantities.

Physical and Chemical Properties

The physical and chemical properties of the four organophosphorus insecticides are included in the attached worksheets. Since demeton contains a mixture of 0,0-diethyl 0-(and S-) ethyl-2-thioethyl phosphorothioates, individual property worksheets for the thiono-isomer and the thiol-isomer are also attached.

2. TOXICOLOGY

All the organophosphorus insecticides function by the common mechanism of cholinesterase inhibition. The enzyme cholinesterase is an essential constituent of the nervous system not only of the Insecta but also of all higher animals, and when inhibited is no longer able to carry out its normal function of rapid removal and destruction of the neurohormone acetylcholine from the nervous synapse. As a result, acetycholine accumulates and disrupts the normal functioning of the nervous system, giving rise to the typical cholinergic systems associated with O-P poisoning. In insects the poisoning leads to hyperactivety, tremors, convulsions, paralysis, and death. In higher animals, these cholinergic effects are translated into muscarinic effects such as nausea, salivation, lacrimation and myosis; nicotinic effects such as muscular fasciculations, and central effects such as giddiness, tremulousness, coma, and convulsions.[0509] The symptoms of poisoning are usually rapid in onset, and death caused by respiratory failure can occur within a few minutes to several hours following exposure. In cases of oral ingestion death has been essentially instantaneous.

The four organophosphorus insecticides included in this Profile Report are all highly toxic and exhibit similar toxicity symptoms, although the toxicity of methyl parathion for higher animals is somewhat lower and both methyl parathion and Guthion penetrate the skin with greater difficulty than parathion or demeton. All four organophosphorus insecticides can be absorbed through the skin and excessive skin contact can lead to death. Special precautions should be taken to prevent both skin contamination and inhalation.

The relative acute oral and dermal LD_{50} values of the four organophosphorus insecticides to the rat range from 2 to 14 mg/kg and 7 to 220 mg/kg and are representative of the hazards associated with the use of specific insecticides (Table 2). Demeton contains both the thiol-isomer and the thiono-isomer, and the thiol-isomer has been identified to be far more toxic than the thiono-isomer; the respective acute oral LD_{50} values to the rat are 1.5 and 30 mg/kg.[1618] The American Conference of Governmental Industrial Hygienists 1971 recommended Threshold Limit Values (TLV) for the compounds in mg/M^3 of air are[0225]: parathion, 0.1; methyl parathion, 0.2; demeton, 0.1; Guthion (azinphosmethyl) 0.2.

The 48-hour median tolerance limits (TL_m) for the organophosphorus insecticides for various types of fresh water organisms have been established by the Federal Water Pollution Control Administration (Table 3). To provide reasonably safe concentrations of these materials in receiving waters, application factors of 1/100 should be used with these values. Another comparision of the toxicity of the organophosphorus insecticides to fish life are their 96-hour TL_m values for the bluegill sunfish in mg/liter: parathion, 0.095; methyl parathion, 1.9; Guthion, 0.0052.[1611] These data indicate that Guthion is the most toxic of the organophosphorus insecticides to fish life, and possibly to other forms of aquatic life.

Most of the organophosphorus insecticides do not accumulate in animal tissues. However, Guthion has been found in fish several weeks after being exposed in laboratory experiments to sub-lethal concentrations in water.

TABLE 2

ACUTE ORAL AND DERMAL LD_{50} VALUES OF ORGANOPHOSPHORUS INSECTICIDES FOR WHITE RATS[1277]

Insecticides	Oral LD_{50} (mg/kg)		Dermal LD_{50} (mg/kg)	
	Males	Females	Males	Females
Parathion	13	3.6	21	6.8
Methyl Parathion	14	24	67	67
Demeton	6.2	2.5	14	8.2
Guthion	13	11	220	220

TABLE 3

48-HOUR TL_m VALUES FROM STATIC BIOASSAY

(in micrograms per liter)[0536]

Insecticides	Stream Invertebrate Species	TL_m	Cladocerans Species	TL_m	Fish Species	TL_m	Gammarus Lacustris TL_m
Parathion	P.Californica	11	D. pulex	0.4	Bluegill	47	6
Methyl Parathion	-------------		D. magna	4.8	Bluegill	8000	----
Demeton*	-------------		D. pulex	14	Bluegill	8181	----
Guthion	P.Californica	8	D. magna	0.2	Rainbow t.	10	0.3

* This is listed as demelton in the orginial table.

3. OTHER HAZARDS

Parathion and metyl parathion are unstable to heat. Parathion should not be heated above 100 C, and methyl parathion may explode at 120 C. For an adequate safety margin, methyl parathion should not be heated above 55 C.[1615] When heated to decomposition, all four organophosphorus insecticides emit highly toxic fumes of nitrogen oxides, phosphorus, and sulfur compounds.

The fire hazards of organophosphorus insecticides are relatively slight and are far outweighed by their health hazards. Parathion has a flash point of about 120 C, and 80 percent methyl parathion in xylene has a flash point of 46 C. The hazards from fires involving organophosphorus insecticides have been investigated[0315] and it was concluded that: first, most of the insecticide is destroyed by decomposition before it can evaporate; second, over 90 percent of the evaporting insecticide is destroyed by the flames; and third, the evaporating portion is considerably diluted by the time it reaches anyone. When all these factors are considered, it is apparent that a fire involving tons of organophosphorus insecticides may occur without causing serious injury to anyone nearby.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Great care should be exercised in handling the organophosphorus insecticides because of their high toxicity and the dangers of absorption through the skin. The use of rubber gloves, goggles, a respirator, and other protective clothing is advisable. Any material spilled on the skin should be immediately removed with plenty of water and soap. If clothing has been contaminated, it should be removed as soon as possible and the skin washed as above.[1615] Periodic examination of blood cholinesterase levels is also of value in the early detection of over-exposure.

Organophosphorus insecticides should be stored in well ventilated areas in a separate building, away from any foodstuffs, feeds, or any other material intended for consumption by humans or animals.[1615] In addition, they should not be stored near sources of heat such as furnaces, heating kettles, and steam lines. Ample warning signs should be posted in storage areas.

Adequate procedures for the transportation of parathion and methyl parathion have been established by the Department of Transportation.[0766] Label requirements, as well as the maximum quantites permitted to be shipped in one outside container, are also specified. Although shipping regulations for demeton and Guthion are not specifically mentioned in the reference, the same rules governing the transportation of the parathions should also apply here.

The National Agricultural Chemicals Associations has established a Pesticide Safety Team Network with Area Coordinators throughout the country to provide nationwide 24-nour emergency service. The network became operational on March 9, 1970 (with a central telephone number: [513] 916-4300) and should be consulted in all cases of accidents, spills, leakage, fires, and other types of disasters involving organophosphorus insecticides.

Disposal/Reuse

Contaminated or degraded organophosphorus insecticides could not be practically considered for reprocessing. The safe disposal of the insecticides is defined in terms of provisional limits in the atmosphere and a potable water source and/or marine habitat. The provisional limits are as follows:

Contaminant in Air	Provisional Limits	Basis for Recommendation
Parathion	0.001 mg/M^3	0.01 TLV
Methyl Parathion	0.002 mg/M^3	0.01 TLV
Demeton	0.001 mg/M^3	0.01 TLV
Guthion	0.002 mg/M^3	0.01 TLV

Contaminant In Water and Soil	Provisional Limits	Basis for Recommendation
Parathion	0.005 ppm (mg/l)	Stokinger & Woodward Method
Methyl Parathion	0.01 ppm (mg/l)	Stokinger & Woodward Method
Demeton	0.005 ppm (mg/l)	Stokinger & Woodward Method
Guthion	0.01 ppm (mg/l)	Stokinger & Woodward Method

The recommended criterion for release of the organophosphorus insecticides to the water environment is so low that none of these insecticides (with the possible exception of methyl parathion) should be applied directly in or near the marine habitat without danger of causing damage. To meet the provisional limits, effluents from plants treating waste water containing the organophosphorus insecticides must normally be diluted in municipal sewers (with an approximate dilution ratio of 10:1) or large creeks or holdings ponds before discharge to lakes, rivers, or oceans.

The permissible criteria for the organophosphorus insecticides in the surface water for public water supplies, however, is much higher and the limit* established relative to parathion is expressed as 0.1 mg/liter parathion equivalent.[0536] This equivalence is the ratio that a given cholinergic insecticide has to parathion as unity in its cholinesterase inhibiting properties.

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* These limits have been set with relation only to human intake directly from a related domestic water supply and do not take into account the consequence of higher and possible objectionable concentrations in fish available to be eaten by man.

5. EVALUATION OF CURRENT AND NEAR FUTURE DISPOSAL PROCESSES

Dilute Pesticide Wastes

Option No.1 - Adsorption with Powdered Activated Carbon.* The effectiveness of powdered activated carbon on the removal of parathion from water has been reported by Robeck et al[0441] and Sigworth.[1635] Robeck et al investigated initial parathion concentrations ranging from about 1 to 10 ppb and found that over 99 percent of the parathion could be removed with powdered activated carbon dosages of 5 to 20 ppm. Sigworth's studies were conducted with higher initial parathion concentrations of 10 ppm and concluded that 5 ppm carbon dosages in a treatment plant could be expected to give 75 percent removal, whereas dosages of 10 ppm would accomplish 90 percent removal of most of the pesticides in extensive use today. The necessary carbon dosage and the associated degree of removal for methyl parathion, demeton, and Guthion should be in the same range as those for parathion. Although the addition of powdered activated carbon to a liquid solution followed by stirring and filtration is not necessarily the best method when large quantities of aqueous wastes have to be dealt with, the procedure is indeed an adequate and acceptable technique for treating dilute organophosphorus pesticide wastes.

Option No.2 - Adsorption with Granular Activated-Carbon Beds.* The effectiveness of granular activated-carbon beds to remove parathion from water has also been investigated by Robeck et al.[0441] Following passage through two carbon columns, it was found that the parathion concentration in water was reduced from 11.4 ppb to 0.05 ppb. Treatment of waste water containing a variety of pesticide wastes with granular activated-carbon bed have been practiced by Fisons Pest Control Ltd., in England since 1955,[1035,1631] where over 99 percent removal of the pesticides is obtained. The treated effluent is diluted with river water before discharge to the river, and the results of government biological surveys indicated no effects of the discharge on the river. Chemagro's organophosphorus pesticide plant at Kansas City, Missouri, which also manufactures demeton and Guthion, is at the present considering the installation of granular activated-carbon beds for the treatment of waste water generated at the plant.[1619] Because of the adequate contact time provided and the fact that it is a well established chemical engineering unit operation, adsorption with granular activated-carbon beds should be considered as one of the most satisfactory methods for treating dilute organophosphorus pesticide wastes.

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* The contaminated carbon may be regenerated in a multi-hearth furnace under a controlled atmosphere at temperatures in excess of 1,600 F, so that the adsorbed impurities are voltalized and selectively oxidized from the surface of the carbon.

Option No.3 - Alkaline Hydrolysis. All the four organophosphorus insecticides considered in this Profile Report are readily hydrolyzed in alkaline medium. Ketelaar reported the hydrolysis constants of parathion and methyl parathion in alkaline solution at 15 C as 0.00215 and 0.0092 liter min^{-1} mol^{-1}, respectively.[1613] The actual reaction rate is bimolecular and depends on the hydroxyl ion concentration in the solution. The half life times for parathion and methyl parathion in a 1 N hydroxide solution are 32 min and 7.5 min respectively. According to Melnikov,[1618] the time for 50 percent hydrolysis of the thiono-isomer of demeton at 20 C and pH 13 is 75 min and that of the thiol-isomer is 0.85 min. The hydrolysis rate of Guthion in alkaline medium is not available directly, although Melnikov[1618] indicates at pH 5 50 percent of the Guthion is hydrolyzed at 20 C in 240 days and that in alkaline solution Guthion breaks down several times faster. From this information, it is apparent that alkaline hydrolysis in a properly designed mixing tank with sufficient residence time is an adequate process for treating dilute parathion, methyl parathion, and demeton wastes. The Kerr-McGee Los Angeles Plant, which manufactures parathion and methyl parathion, treats its waste water by alkaline hydrolysis in a tank followed by a holding lagoon before discharge to the municipal sewer.[1529]

Option No.4 - Activated Sludge Treatment. Stutz[1037] and Coley and Stutz[1039] reported the biological treatment of waste water containing parathion and methyl parathion manufacturing wastes by the activated sludge process at Monsanto's Anniston, Alabama plant. The processing steps for waste treatment involve chlorination, holding in a raw waste lagoon, limestone neutralization, and pH adjustment with soda ash or caustic before feeding to the activated sludge unit. Plant effluent analysis indicates parathion concentrations less than 0.1 mg/liter, and since the effluent is discharged into a relatively large creek (with an approximate dilution ratio of 100:1) and then to a river, a factor of safety for fish toxicity of at least 100:1 is provided. The biological treatment of waste waters containing demeton and Guthion with an aerated lagoon preceding the activated sludge unit has been investigated by Lue-Hing and Brady on the pilot scale,[1036] and the system developed was found to be totally effective for detoxification. As a result of the successful study, a full scale design with a two-stage activated sludge process has been proposed as the secondary waste water treatment unit at Chemagro's Kansas City, Missouri organophosphorus pesticide manufacturing facility. As of today, however, Chemagro is still conducting studies with a 1/5 full scale aeration tank in its secondary waste water treatment effort.[1619] With proper biological acclimation, the activated sludge process preceded by the necessary primary waste treatment steps is an adequate and satisfactory method for treating dilute organophosphorus pesticide wastes.

Option No.5 - Removal by Surface Active Agents. The removal of pesticides from water by the use of surface active agents to produce a foam has been investigated by Whitehouse.[0445] Although organophosphorus pesticides were not included in the study, the results with aldrin and dieldrin showed that up to 90 percent removal was attainable and demonstrated the value of the process as a possible treatment method for other types of pesticides.

The other treatment processes for the removal of organophosphorus insecticides from water that have been investigated include coagulation followed by sand filtration, and chemical oxidation with chlorine, potassium permanganate, and ozone.[0441] Organophosphorus insecticides are not removed by coagulation and filtration, and in the case of parathion, chemical oxidation will sometimes render the more toxic paraoxon as a product. These processes are therefore considered as inadequate methods for treating dilute organophosphorus pesticide wastes.

Concentrated Pesticide Wastes

Option No.1 - Incineration. The complete and controlled high temperature oxidation of organophosphorus insecticides in air or oxygen with adequate scrubbing and ash disposal facilities offers the greatest immediate potential for the safe disposal of these pesticides. The research on incineration of pesticides conducted by Kennedy et al at Mississippi State University has led to the conclusion that temperatures at or near 1,800 F will be sufficient to degrade 99 percent or more of most reagent-grade pesticides and commercial pesticidal formulations.[0062, 0063] It is expected that either a rotary kiln or liquid combustor, depending upon the form of the waste, followed by secondary combustion and scrubbing would be an acceptable disposal method. Primary combustion should be carried out at a minimum of 1,500 F for at least 0.5 seconds with secondary combustion at a minimum temperature of 2,200 F for at least 1.0 second. The equilibrium product distributions resulting from the thermal decomposition and combustion of parathion at atmospheric pressure and three temperatures, 2,190 F (1,200 C), 1,470 F (800 C), 930 F (500 C), have been computed using the TRW Chemical Analysis Program (Table 4), and the results indicate the possible formation of objectionable combustion products such as hydrogen sulfide* and phosphorus oxides. As the same combustion products will be obtained in the incineration of the other three organophosphorus insecticides, an adequate gas clean up system must be installed to alleviate the air pollution problem. Monsanto's Anniston, Alabama parathion and methyl parathion manufacturing facility uses incineration to dispose of its semi-solid residue wastes, and has proven that an aqueous scrubbing system followed by a mist eliminator is effective in recovering 99.9 percent of the phosphorus pentoxide.[1037]

---

* A higher air/fuel ratio will lead to the formation of sulfur dioxide instead of hydrogen sulfide.

TABLE 4

EQUILIBRIUM COMPOSITION OF PARATHION/AIR SYSTEM

(1 Atm Pressure) MOLE FRACTION, GAS PHASE*+†

Wt. % Pesticide	Temp.	CH_4	CO	CO_2	H_2	H_2O	HCN	H_2S	N_2	P_4O_6	Condensed Phase Graphite Mol/100G Feed
100	1200 C	6.584-4	3.784-1	1.229-4	4.795-1	3.834-4	1.572-4	5.140-2	3.025-2	-	1.693
	800 C	1.224-2	2.812-1	1.129-2	5.142-1	1.890-2	-	9.095-2	4.631-2	2.316-2	2.298
	500 C	1.460-1	1.983-2	9.855-2	2.568-1	2.467-1	-	1.322-1	6.622-2	3.314-2	2.748
70	1200 C	3.384-4	3.693-1	1.171-4	3.438-1	2.683-4	3.417-4	3.538-2	1.993-1	-	0.740
	800 C	5.736-3	2.937-1	1.230-2	3.520-1	1.351-2	-	6.082-2	2.446.1	1.564-2	1.199
	500 C	6.884-2	2.170-2	1.181-1	1.764-1	1.854-1	-	8.288-2	3.254-1	2.081-2	1.800
50	1200 C	1.795-4	3.632-1	1.132-4	2.504-1	1.921-4	3.700-4	2.424-2	3.208-1	-	0.105
	800 C	2.854-3	3.020-1	1.301-2	2.483-1	9.799-3	-	4.195-2	3.695-1	1.092-2	0.461
	500 C	3.465-2	2.319-2	1.347-1	1.251-1	1.405-1	-	5.545-2	4.719-1	1.395-2	1.123
20	1200 C	-	8.885-2	1.109-1	3.222-2	9.896-2	-	9.140-3	6.484-1	5.013-3	-
	800 C	-	6.655-2	1.342-1	4.287-2	7.917-2	-	1.913-2	6.521-1	5.042-3	-
	500 C	5.524-3	2.581-2	1.669-1	4.996-2	6.245-2	-	2.017-2	6.637-1	5.132-3	0.022

---

*Small amounts of CS_2, COS, P_2, P_4, and S_2 are also present at 1200 C.

+The data format used is an exponential form, i.e., X.XX-Y is equivalent to X.XX 10^{-Y}

†Mole fractions less than 10^{-4} are indicated by -.

The other major air pollutant of concern, sulfur dioxide, is undoubtedly removed by the same system. Properly designed and operated incineration is therefore considered as the best present and near future method for the disposal of concentrated organophosphorus pesticide wastes.

Option No.2 - Chemical Degradation. The use of chemical reagents to decompose concentrated pesticide wastes to less toxic forms has also been investigated by Kennedy et al.[0062,0063] The Mississippi State work has shown that: (1) sulfuric and nitric acids are not effective in destroying the organophosphorus pesticide malathion; (2) sodium hydroxide from 2N to 8N concentration will break down malathion sufficiently to yield inorganic phosphates; and (3) liquid ammonia and metallic sodium or lithium will completely decompose malathion, but the reagents are dangerous to use and the toxicity of the degradation products are not known. Based on the results to date, treatment with sodium hydroxide is the only recommended chemical method for the disposal of concentrated organophosphorus pesticide wastes.

Option No.3 - Sanitary Landfill. Soil burial of organophosphorus pesticide wastes, because of their relatively short persistence time in soil of one to three months,[0206,0488] is a satisfactory means of disposal provided the site is acceptable from a geologic and ground water hydrology standpoint and has been approved as a sanitary landfill by appropriate authorities.[0620] The practice of disposing large quantities of concentrated pesticides at any one sanitary landfill site, however, is not recommended.[0448]

Option No.4 - Deep Well. Although a properly planned, properly designed, properly constructed, and properly operated deep well disposal installation is an expensive investment, it may still be the only economic alternative for pesticide manufacturers and large formulators to dispose of large volumes of pesticide wastes from productive operations. However, the method is uneconomical for the occasional disposal of small volume pesticide wastes. The solubility in water of the four organophosphorus insecticides considered in this report are: parathion, 24 ppm; methyl paration, 50 ppm;

demeton, 60 ppm; Guthion, 30 ppm. Because of the potential contamination of ground water, deep well disposal of organophosphorus pesticide wastes is not recommended by the National Working Group on Pesticides,[0620] and the method should be considered only under very special situations where hazards would be nonexistent.

The disposal of organophosphorus pesticide wastes in open pits, lagoons, unapproved landfill sites, and by on-site burning or deep-sea burial are not recommended practices because of the obvious contributions to air and water pollution.

To summarize, the adequate methods for treating dilute organophosphorus insecticides are: (1) adsorption with powdered activated carbon; (2) adsorption with activated-carbon beds; (3) alkaline hydrolysis (except for Guthion); and (4) activated sludge treatment. The adequate methods for the disposal of concentrated organophosphorus pesticide wastes are: (1) incineration; (2) chemical degradation with 2N to 8N sodium hydroxide solution; and (3) approved sanitary landfill.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is anticipated that disposal systems to handle both dilute and concentrated organphosphorus pesticide wastes will be required at National Disposal Sites located near pesticide manufacturers, formulators, and users and especially agriculture centers. The dilute pesticide wastes that will require treatment will include spent cleaning solutions for pesticide containers and any other pesticide contaminated waste water. The concentrated pesticide wastes that will require treatment include any surplus, contaminated, partially or fully degraded pesticides.

The process recommended for the treatment of dilute organophosphorus pesticide wastes at National Disposal Sites are:

Process	Order of Preference	Remarks
Activated-carbon Beds	First choice	Demonstrated technology; also adequate for removal of most other types of pesticides from waste water.
Activated Sludge	Second Choice	Demonstrated technology; however, other types of pesticides in waste water may be toxic to bacteria specially acclimated for treating organophosphorus wastes.
Alkaline Hydrolysis	Third Choice	Demonstrated technology; but not applicable to pesticides that are not readily hydrolyzed in alkaline medium such as Guthion.

The only process recommended for treating concentrated organophosphorus pesticide wastes at National Disposal Sites is incineration. Both chemical degradation with strong alkaline solution and sanitary landfill are not considered suitable for the disposal of large volumes of concentrated pesticide wastes.

It should be noted that the activated-carbon bed and the activated sludge processes are also applicable to the treatment of other types of dilute organophosphorus pesticide wastes, such as TEPP and malathion wastes. To treat other types of concentrated organophosphorus pesticide wastes, incineration is again the only recommended process.

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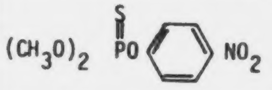
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Methyl Parathion (274)

IUC Name 0,0-dimethyl 0-p-nitrophenylphsophorothioate

Common Names 0,0-dimethyl 0-4-nitrophenylthiophosphate

Structural Formula



$(CH_3O)_2\overset{S}{\overset{\|}{P}}O-C_6H_4-NO_2$

Molecular Wt. 263.21(1)   Melting Pt. 36 C(2)   Boiling Pt. ____

Density (Condensed) 1.358 @ 20 C(2) Density (gas) ____ @ ____

Vapor Pressure (recommended 55 C and 20 C)

0.05 mm @ 109 C(2) 0.97×10^{-5} mm @ 20 C(2)   ____ @ ____

Flash Point 46 C (commercial product)   Autoignition Temp. ____

Flammability Limits in Air (wt %)   Lower ____   Upper ____

Explosive Limits in Air (wt. %)   Lower ____   Upper ____

Solubility

Cold Water 55 mg/liter at 25 C(2)   Hot Water ____   Ethanol ____

Others: xylene

Acid, Base Properties ____

Highly Reactive with heat and may explode at temperatures above 120 C

Compatible with ____

Shipped in one to ten gallon cans and 55 gallon steel drums

ICC Classification Poison B   Coast Guard Classification Poison B

Comments A white solid, commercial methyl parathion is a liquid consisting of 80% methyl parathion and 20% xylene. Decomposes at temperatures above ambient and may develop sufficient internal pressure to cause the container to rupture violently.

References (1) 0766
(2) 1618
(3) 1615

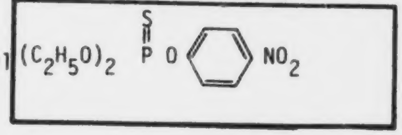
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Parathion (321)

IUC Name 0,0-diethyl 0.p-nitrophenylphosphorothioate

Common Names Ethyl Parathion, 0,0-diethyl 0-4-nitrophenyl thiophosphate

Structural Formula



$(C_2H_5O)_2$

Molecular Wt. 291.27(1) Melting Pt. 6 C(2) Boiling Pt. 375 C(1)

Density (Condensed) 1.26 @ 25/4 C Density (gas) ______ @ ______

Vapor Pressure (recommended 55 C and 20 C)

0.57×10^{-5} mm @ 20 C(2) 0.6 mm @ 157-162 C(1) ______ @ ______

Flash Point ______ Autoignition Temp. ______

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water 24 mg/liter(2) Hot Water ______ Ethanol soluble

Others: benzene, xylene, phthalates, glycols, esters, hetones. toluene, chloroform, carbon tetrachloride, animal and vegetable oils(1)

Acid, Base Properties ______

Highly Reactive with heat, parathion should not be heated above 100 C and may explode at higher temperatures(2)

Compatible with ______

Shipped in one to ten gallon cans and 55 gallon steel drums

ICC Classification Poison B Coast Guard Classification Poison B

Comments Yellowish liquid. It emits highly toxic fumes of nitrogen oxides, phosphorus and sulfur when heated to decomposition.

References (1) 1492
(2) 1618
(3) 1615

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Demeton (491)

IUC Name 0,0-diethyl 0-(and S-) ethyl-2-thioethyl phosphorothioates

Structural Formula

$(C_2H_5O)_2$ PSO $CH_2CH_2SC_2H_5$

Common Names Systox, E-1059

Molecular Wt. 258.34(1) Melting Pt. ______ Boiling Pt. ______

Density (Condensed) 1.1183(2) @ ______ Density (gas) ______ @ ______

Vapor Pressure (recommended 55 C and 20 C)

2mm @ 134 C(2) ______ @ ______ ______ @ ______

Flash Point ______ Autoignition Temp. ______

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water ______ Hot Water ______ Ethanol ______

Others: soluble in organic solvents

Acid, Base Properties ______

Highly Reactive with ______

Compatible with ______

Shipped in one to ten gallon cans and 55 gallon steel drums

ICC Classification Poison B Coast Guard Classification ______

Comments Demeton is a mixture of two parts of the thiono isomer and one part of the thiol isomer of 0,0-diethyl 2-ethyl-mercaptoethyl thiophosphate. It is usually marketed in the form of 30 and 50% emulsive concentrates.(2)

References (1) 1492

(2) 1617

(3) 1618

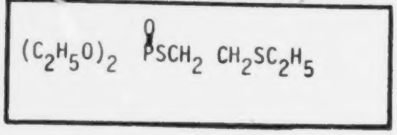
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Demeton (thiol-ismoer) (491)

IUC Name 0,0-diethyl S-2-(ethylthio)-ethyl
Phosphorothioate

Common Names Systox (thiol-isomer)
0,0-diethyl S-2-ethyl mercaptoethyl
thiophosphate

Structural Formula



$(C_2H_5O)_2\overset{O}{P}SCH_2\ CH_2SC_2H_5$

Molecular Wt. 258.34(1) Melting Pt. ______ Boiling Pt. ______

Density (Condensed) 1.132(2) @ ______ Density (gas) ______ @ ______

Vapor Pressure (recommended 55 C and 20 C)

1 mm @ 128 C(2) 0.25 nn @100 C(3) 2.6 X10^{-4}mm @ 20 C(3)

Flash Point ______ Autoignition Temp. ______

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water 0.02-0.2%(2) Hot Water ______ Ethanol ______

Others: Highly soluble in most organic solvents

Acid, Base Properties ______

Highly Reactive with ______

Compatible with ______

Shipped in ______

ICC Classification Poison B Coast Guard Classification ______

Comments Colorless oil

References (1) 1492
(2) 1617
(3) 1618

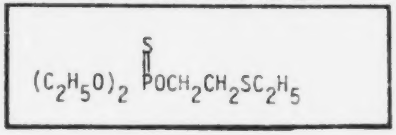
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Demeton (thiono-isomer)(491)

IUC Name 0,0-diethyl 0-2 (ethylthio)-ethyl phosphorothioate

Common Names 0,0-diethyl 0-2-ethyl mercaptoethyl thionophosphate, systox (thiono-isomer)

Structural Formula



$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}OCH_2CH_2SC_2H_5$

Molecular Wt. 258.34(1) Melting Pt. ____ Boiling Pt. ____

Density (Condensed) 1.119(2) @ ____ Density (gas) ____ @ ____

Vapor Pressure (recommended 55 C and 20 C)

1 mm @ 123 C(2) 2.5 X10^{-4} mm @ 20 C(3) 0.4 mm @ 106 C(3)

Flash Point ____ Autoignition Temp. ____

Flammability Limits in Air (wt %) Lower ____ Upper ____

Explosive Limits in Air (wt. %) Lower ____ Upper ____

Solubility

Cold Water 0.002-0.02%(2) Hot Water ____ Ethanol ____

Others: Highly soluble in organic solvents, including the petroleum hydrocarbons.

Acid, Base Properties ____

Highly Reactive with Isomerizes very readily to form the thiol-isomer

Compatible with ____

Shipped in ____

ICC Classification Poison B Coast Guard Classification ____

Comments A colorless liquid when pure

References (1) 1492
(2) 1617
(3) 1618

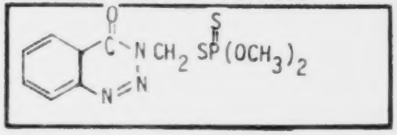
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Guthion (495)

IUC Name 0,0 dimethyl S-(1,2,3-benzotriazinyl-4-keto)-3-methyl phosphorodithioate

Common Names Azinphosmethyl

Structural Formula



Molecular Wt. 317.34(1) Melting Pt. 73-74C(1) Boiling Pt.

Density (Condensed) 1.44(1) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

2.2×10^{-7} mm @ 20 C(2) @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.003 %(2) Hot Water Ethanol soluble (1)

Others: soluble in methanol, propylene glycol, xylene and other organic solvents(1)

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in one to ten gallon cans and 55 gallon steel drums

ICC Classification Poison B Coast Guard Classification

Comments A white solid(1). It is usually marketed in the form of emulsive concentrates and wettable powders for spraying in aqueous solutions.(2)

References (1) 1492
(2) 1618

PROFILE REPORT

Dinitro Cresol (162)

1. GENERAL

Introduction

Dinitro cresol (4,6-dinitro-o-cresol, DNOC) belongs to the class of dinitrophenol compounds with a wide range of biocidal action and are useful as insecticides, acaricides, herbicides, and fungicides. Potassium dinitro-o-cresylate, marketed in Germany in 1892, was the first synthetic organic insecticide. The compounds in use today are all derivatives of 4,6-dinitro-2-alkylphenols and their salts or esters.

Current production of DNOC is only at the rate of 20,000 to 30,000 lb/year,[1964] and indications are that it is being displaced more and more by its homologs, and primarily by 2,4-dinitro-6-sec-butylphenol (DNBP, dinoseb). DNBP has the advantages of being less explosive, somewhat less toxic to man and domestic animals, and more effective in controlling plant pests, plant diseases, and weeds. DNBP surpasses DNOC almost three times in insecticidal and herbicidal effect, and because of the lower dosage, the cost of treatment per unit of area is substantially lower. Less of the DNBP compound remains on the plants, and the hazard in using it is decreased. Although this Profile Report is principally concerned with DNOC, the waste management techniques discussed will also be generally applicable to DNBP.

Manufacture

DNOC is produced by the direct nitration of o-cresol with a nitrating mixture at a low temperature, or in some cases, the o-cresol is first sulfonated with concentrated sulfuric acid before the nitration.

Blue Spruce Company, Basking Ridge, New Jersey, is the only U.S. manufacturer of technical grade DNOC.[1964]

Uses

DNOC is used in agriculture to control plant pests and diseases, and for the treatment of fruit trees before opening of the buds, either in the form of emulsions with oils or more often in the form of aqueous solutions of its salts. In the control of weeds DNOC is used exclusively in the form of aqueous solutions of the salts, and good results are obtained in weed control in plantings of flax, grains, and some other crops.[1618]

Sources and Types of Pesticide Wastes

The sources of pesticide wastes may include the following[0620]: (1) pesticide manufacturers; (2) pesticide formulators; (3) pesticide wholesalers; (4) professional applicators; (5) cooperage facilities that recondition drums; (6) agricultural users; (7) government facilities that store, transport, and use pesticides; (8) urban and suburban home garden users; (9) commercial and industrial processes including those from rug and fabric treatment facilities manufacturing plants, hospitals, etc.

In general, pesticide wastes can be classified as either diluted or concentrated wastes. Diluted pesticide wastes include those generated in the waste waters of the manufacturers, formulators, agricultural runoffs, and possibly spent caustic solutions used to clean empty pesticide containers. Concentrated pesticide wastes include any unused or contaminated pesticides, pesticide materials left in containers after emptying, sludges formed in treating waste water containing pesticides, sawdust or straw used to soak up accidental pesticide spills.

Physical and Chemical Properties

The physical and chemical properties of DNOC are described in the attached worksheet.

2. TOXICOLOGY

The dinitrophenols are biologically active because of their ability to uncouple oxidative phosphorylation. As a result insects poisoned by DNOC undergo pronounced increases in the rate of respiration, which may reach 3 to 10 times normal, and they die from metabolic exhaustion because of their inability to utilize the energy provided by respiration and glycosis for the conversion of ortho-phosphate to high energy phosphate bonds.[0509]

DNOC is also highly toxic to man and animals and a number of fatalities have resulted from its use in medicine, industry, and agriculture. It is an accumulative poison in man and is excreted very slowly. The symptoms of poisoning include a feeling of warmth, excessive perspiration and thirst, general debility and weariness, acute distress, collapse, and death followed by almost instantaneous rigor. Opacity of the lens of the eye has been produced in laboratory animals following chronic poisoning by DNOC and has occurred occasionally in humans taking this compound for reducing purposes in the past.[1617]

The acute oral and dermal LD_{50} values of DNOC to the rat are 30 and 600 mg/kg body weight respectively.[1277] The chronic toxicity of DNOC has also been extensively studied, and it was established that a DNOC concentration of 100 ppm can be tolerated in the diet with no measurable effects.[0509,1617]

The American Conference of Governmental Industrial Hygienists (ACGIH) 1971 recommended Threshold Limit Value (TLV) for DNOC in air is 0.2 mg/M^3.[0225]

The 48-hr Median Tolerance Limits (TL_m) for DNOC established by the Federal Water Pollution Control Administration for various types of fresh water organisms in micrograms per liter are[0509]: P. Californica (stream invertebrate), 560; and Rainbow trout (fish), 210. These data are indicative of the hazards to aquatic life associated with the use of DNOC.

3. OTHER HAZARDS

DNOC forms highly water soluble salts with caustic alkalies, ammonia, and organic amines, and these salts, when in the dry state, explode readily from shock or detonation.[1618]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Transportation, and Storage

DNOC is highly toxic and is rapidly absorbed through the intact skin when used in the form of oil solutions. Work with DNOC should be carried out with the strict observance of necessary precautionary measures, and the use of rubber gloves, goggles, a respirator, and other protective clothing is advisable. Special care should be exercised in handling the salts of DNOC because of their explosive nature.

DNOC should be stored in cool, dry, well ventilated places and away from any area where the fire hazard may be acute. Outside or detached storage is preferred. Proper warning signs should be posted in storage areas.[1616]

DNOC is classified as a Class B poison by the Department of Transportation and the rules governing its transportation are given in the Code of Federal Regulations (CFR) Title 49--Transportation, Parts 71-90.[0278]

The National Agricultural Chemicals Association has established a Pesticide Safety Team Network with Area Coordinators throughout the country to provide nationwide 24-hr service. The network became operational on March 9, 1970 (with a central telephone number [513] 916-4300) and should be consulted in all cases of accidents, spills, leakage, fires, and other types of disasters involving DNOC.

Disposal/Reuse

Contaminated or degraded DNOC could not be practically considered for reprocessing. The safe disposal of the pesticide is defined in terms of the recommended provisional limits in the atmosphere and potable water source and/or marine habitat. The recommended provisional limits are as follows:

Contaminant and Environment	Provisional Limits	Basis for Recommendation
DNOC in air	0.002 mg/M^3	0.01 TLV
DNOC in water and soil	0.01 ppm(mg/l)	Stokinger and Woodward method.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Dilute Pesticide Wastes

Option No.1 - Adsorption with Granular Activated-Carbon Beds. Treatment of waste water containing DNOC with activated-carbon columns has been practiced by Fisons Pest Control Ltd., in England since 1955,[1035,1631] where over 99 percent removal of the pesticide is obtained. There are six adsorption towers, each 7 ft 6 in. in diameter and 25 ft high overall, capable of containing 7 to 10 tons of activated carbon. The activated carbon employed is normally 10 to 20 B.S.S. mesh and the flow rate through the towers normally 3,000 gal/hr, and the spent carbon is reactivated in a conventional rotary furnace. The nominal concentrations of DNOC in the plant effluent are 60 to 190 ppm before treatment and 0.1 to 0.6 ppm after treatment. The treated effluent is diluted with river water before additional treatment in trickling filters and an aeration system followed by discharge to river. No further removal of DNOC from the waste water is observed in the biological treatment stages, but the results of governmental biological surveys indicated no effects of the discharge on the river thus indicating the adequacy of the activated-carbon treatment by itself. Because of the proven capability and the fact that it is a well established chemical engineering unit operating, adsorption with granual activated-carbon beds should be considered as one of the most satisfactory methods for treating dilute DNOC wastes.

Option No.2 - Adsorption with Powdered Activated Carbon. Although the use of powdered activated carbon to remove DNOC from water has not been investigated directly, the effectiveness of DNOC adsorption with granular activated-carbon beds and the results of the related studies on powdered activated carbon adsorption of other pesticides conducted by Robeck et al,[0441] Sigworth,[1635] and Whitehouse[0445] indicate that the addition of powdered activated carbon to a liquid solution followed by stirring and filtration is an adequate method for treating dilute DNOC wastes.

Option No.3 - Biological Degradation. Southern Dyestuff Company, Charlotte, North Carolina, has demonstrated on the pilot plant scale that waste waters containing nitrophenols could be successfully treated in an activated sludge unit,[1450] and is presently in the process of installing a complete waste treatment facility including an activated sludge unit, an aeration system, and a chlorination stage to handle their manufacturing waste streams.[1805] In the opinion of Southern Dyestuff, waste waters containing DNOC could also be adequately treated by the same system.[1805]

Option No.4 - Eli Lilly Process. R.H.L. Howe of Eli Lilly and Company has developed a patented process for removing nitrophenols and nitroanilines from waste waters.[0534] The process consists of acidifying the waste stream to a pH of less than about three, adding an absorbent material to take up the colored components, adding a metallic oxide or hydroxide to adjust the pH to more than about five and also to form a precipitate, and separating the mixture into an effluent and a sludge or foam (scum). The resulted effluent is free of nitrophenols and nitroanilines and can then be treated by conventional techniques. According to Howe,[1802, 1974] the process is also applicable to the treatment of waste waters containing 100 ppm to a few weight percent DNOC, and the treated effluent would be non-toxic to fish life and safe to any receiving sewer or water course.

Option No.5 - Light Catalyzed Chlorine Oxidation. The effect of ultraviolet radiation on the rate and extent of chlorine oxidation of 2,4-dinitrophenol has been briefly investigated by Meiners et al.[0887,1804] The results with initially 38 ppm 2,4-dinitrophenol (15 ppm total organic carbon) indicated the rapid degradation of the compound (practically 100 percent elimination in 8 min) and the fairly rapid decrease in the total organic carbon (53 percent in 10 min), and demonstrated the value of the process as a near future treatment method for dilute DNOC wastes.

Concentrated Pesticide Wastes

Option No.1 - Incineration. The complete and controlled high temperature oxidation of DNOC in air or oxygen with adequate scrubbing and ash disposal facilities offers the greatest immediate potential for the safe disposal of the pesticide. The research on incineration of pesticides conducted by Kennedy et al at Mississippi State University has led to the conclusion that DNBP approached complete combustion at temperatures as low as 600 C and identified carbon monoxide, carbon dioxide, and ammonia as the volatile products from burning of the DNBP formulation at 900 C.[0062,0063] Because of the similarity in chemical structure of DNBP and DNOC, temperatures not far above 600 C should also be sufficient to degrade DNOC and the same combustion products should be obtained. It is expected that either a rotary kiln or liquid combustor, depending on the waste form, followed by secondary combustion and scrubbing would be the best current and near future method for the disposal of concentrated DNOC wastes. Again, primary combustion should be carried out at a minimum of 1,500 F for at least 0.5 second with secondary combustion at a minimum temperature of 2,200 F for at least 1.0 second.

Option No.2 - Chemical Degradation. The use of chemical reagents to decompose concentrated pesticide wastes to less toxic forms has also been investigated by Kennedy et al.[0062,0063] The Mississippi State work showed that: (1) DNBP was altered structurally by sodium hydroxide but the spectrum produced was not resolved; (2) 80 percent of the DNBP were decomposed when treated with the sodium biphenyl reagent prepared by heating a mixture of metallic sodium, anhydrous toluene, and the dimethyl ether of ethylene glycol; (3) 93.8 percent DNBP degradation were obtained when the pesticide was treated with liquid ammonia and metallic sodium. Although liquid ammonia and metallic sodium would probably also completely decompose DNOC, the reagent is dangerous to use and the toxicity of the degradation products are not known. Based on the results to date, chemical degradation could not be recommended as a method for the disposal of concentrated DNOC wastes.

Option No.3 - Sanitary Landfill. Although data is not available on the persistence of DNOC in soil, the pesticide readily forms water soluble ammonium, sodium, potassium, and calcium salts and poses the problem of potential ground and surface water pollution. Sanitary landfill should therefore be considered only for the disposal of small quantities of DNOC wastes, and only at approved sites that are acceptable from a geologic and ground water hydrology standpoint.[0620]

Option No.4 - Deep Well. Although DNOC itself is only sparingly soluble in water, the potential contamination of ground water by the water soluble ammonium, potassium, sodium, and calcium salts of DNOC makes deep well, at best, a questionable method for the disposal of DNOC. Deep well disposal is not recommended by the National Working Group on Pesticides,[0620] and should be considered only under special situations where hazards would be nonexistent.

The disposal of DNOC wastes in open pits, lagoons, unapproved landfill sites, and by onsite burnings or deep-sea burial are not recommended practices because of the obvious contributions to air and water pollution.

To summarize, the adequate methods for treating dilute DNOC wastes are either adsorption with granular activated-carbon beds or adsorption with powdered activated carbon. The only adequate method for the disposal of concentrated DNOC wastes is incineration. Based on the information to date, activated sludge treatment, the Eli Lilly process, and light catalyzed chlorine oxidation could all be considered only as possible near future methods for treating dilute DNOC wastes.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

DNOC and its homologs, because of their relatively high toxicity and widespread use and distribution as a pesticide in the farming communities, are candidate waste stream constituents for National Disposal Site treatment. The recommended unit operation for disposal of dilute dinitrophenol waste is adsorption with activated carbon in either powdered or granular form while the only operation judged adequate for concentrated dinitrophenol waste disposal is controlled incineration.

It should be noted that both the activated carbon and incineration processes are generally applicable to the disposal of most pesticides. They are therefore expected to be utilized at National Disposal Sites which handle pesticides and are located near agricultural centers and pesticide manufacturers.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Dinitro Cresol (162)

Structural Formula

IUC Name 2-4-dinitro-6-methylphenol

Common Names 4,6-dinitro-O-cresol, DNC, DNOC

Molecular Wt. 198.1 Melting Pt. 86.4C(2) Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

5.2×10^{-5} mm @ 25 C(2) @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.0128%(2) Hot Water Ethanol 4.3% at 15 C(3)

Others: very soluble in acetone and benzene

Acid, Base Properties DNOC is a pseudo acid and readily forms water soluble sodium, potassium, calcium and ammonium salts(1)

Highly Reactive with

Compatible with

Shipped in

ICC Classification Poison B Coast Guard Classification

Comments DNOC is a yellow crystalline substance in the pure state.

References (1) 509
(2) 1618
1433
(3)

PROFILE REPORT

Cadmium Cyanide (84), Calcium Cyanide (91), Copper Cyanides (120), Cuprous Cyanide (128), Cyanide (129), Lead Cyanide (239), Nickel Cyanide (295), Potassium Cyanide (344), Silver Cyanide (370), Sodium Cyanide (387), and Zinc Cyanide (457)

1. GENERAL

The cyanides listed above are included in a combined Profile Report because they respond in similar fashion to disposal processes due to the cyanide group present in each of the compounds.

Hydrocyanic acid (215), hydrogen cyanide (218), and mercuric cyanide (254) are not included in this combined Profile Report, but are included in separate reports because of the special disposal problems these compounds present.

The majority of cyanide-containing waste streams are discharged from the electroplating industry and include liquid, slurry, sludge, and solid forms depending upon the degree of concentration. Rinse waters from copper electroplating, for example, may be concentrated by passing through evaporators. In this case, the waste may be a crystalline solid containing 15 percent by weight copper in copper cyanide and sodium cyanide salts (40 percent solids by weight) with traces of other metals. A typical concentrated liquid waste from copper electroplating rinse waters may contain 2 percent copper cyanide, 6 percent sodium cyanide, sodium sulfonate, hydrocarbons and zinc phosphate in 83 percent water.

A characteristic concentrated liquid waste stream containing cyanide wastes from zinc electroplating may be 0.8 percent cyanide in 1 percent sodium hydroxide containing 3300 ppm of zinc and 165 ppm nickel. A characteristic sludge may contain 20 percent sodium ferrocyanide with 2 percent zinc and insolubles, and 50 percent water.

It is estimated that there are 21,323,600 lb of cyanide wastes and 2,106,000 lb of copper wastes generated in the electroplating industry each year. The geographic distribution of these wastes is shown in Volume 14, the volume titled, "Waste Forms and Quantities."

Calcium Cyanide

Pure calcium cyanide is known only in the laboratory. A crude cyanide containing 48 to 50 percent cyanide expressed as sodium cyanide is the only important calcium cyanide of commerce at the present time. It is sold in the form of black or gray flakes, powder, or cast blocks and is known as black cyanide or under trade names such as Aero Brand cyanide, Cyanogas, and Aerocase 28. Physical/chemical properties are summarized in the attached worksheet.

Calcium cyanide is prepared by a process in which calcium cyanamide is caused to react with the carbon present in crude calcium cyanamide in the presence of salt:

$$CaCN_2 + C \xrightarrow{NaCl} Ca(CN)_2$$

The temperature for the reaction, 1,000 C, is attained through the use of an electric furnace. The melt is quick-cooled on a flaking wheel, which rapidly chills the product to prevent reversion to cyanamide. This product is sold in the form of a dark gray flake or is melted and cast into molds for sale as bricks.

The more important uses for black cyanide are as follows:

(1) Cyanidation of Gold and Silver from Ores - Metallic gold and silver dissolve in cyanide solutions in the presence of oxygen to form

the corresponding cyano complexes. The dissolved gold and silver are reprecipitated with zinc dust as a sludge which is refined to obtain pure gold, silver and the other metals present. The zinc added is converted to zinc cyanide which in an alkaline solution, complexes as per the following reaction:[1158]

$$2\ Zn\ (CN)_2 + 4\ OH^- \rightarrow [Zn(CN)_4)]^{2^-} + [Zn(OH)_4]^{2^-}$$

(2) Depressor in Froth Flotation - Black cyanide in solution has the property of rendering certain minerals less amenable to flotation (it depresses zinc in lead-zinc ores, zinc and iron in complex lead-zinc-iron ores, and iron in copper ores).[1158]

(3) Fumigation of Citrus Groves, Greenhouses, etc.[1433]

(4) Commercial Production of Hydrogen Cyanide - Black cyanide is acidified and the evolved hydrogen cyanide-water mixture is concentrated by distillation.

(5) Manufacture of Ferrocyanides.[1433]

(6) Case Hardening of Steels - In case hardening (carburizing), a high carbon surface layer is imported to a low carbon steel by heating up to 1,600 F in a molten bath containing $Ca(CN)_2$, NaCl, CaO, and carbon.[1146]

Cadmium Cyanide

Cadmium cyanide crystallizes as a colorless rhombic crystal. It may be prepared in the laboratory by treating cadmium sulfate with an alkali metal cyanide or by dissolving cadmium hydroxide in aqueous hydrocyanic acid. Its main use is in the form of a complex in electroplating with cadmium for rust protection. Because of high losses during purification, cadmium cyanide is not prepared commercially in dry form, but usually as a solution of sodium cyanocadmate, $Na_2[Cd(CN)_2]$. This is formed by dissolving cadmium oxide in sodium cyanide solution.[1433] Physical/chemical properties are summarized in the attached worksheet.

Copper Cyanides

Copper forms two cyanides, cupric cyanide, $Cu(CN)_2$, and cuprous cyanide, CuCN. Cupric cyanide is a yellow powder which is unstable and rapidly decomposes at ordinary temperatures giving off cyanogen and forming $2\ CuCN \cdot Cu(CN)_2 \cdot 5\ H_2O$. Only the more stable cuprous compound is an item of commerce, and therefore, only this compound will be discussed in this Profile Report.

When pure, cuprous cyanide is a white insoluble compound. Its principal uses are in electroplating, medicine, removal of oxygen from molten metals (particularly copper), insecticides, underwater paint, and organic nitrile separation. In solutions for electroplating of copper, cuprous cyanide is placed in solution by formation of complex ions with excess soluble cyanide.

There are several methods for the preparation of cuprous cyanide.[1433] In one method cupric sulfate solution is reacted simultaneously with aqueous solutions of sodium hydroxide and sodium hydrogen sulfite to reduce the cupric ions. A sodium cyanide solution is then added and the cuprous cyanide precipitated, filtered, washed and air dried. Another preparation method used today is to treat alkali cyanide solution with cuprous chloride. Commercial preparation of cuprous chloride is accomplished by reducing cupric chloride with scrap copper in the presence of hot sodium chloride brine.

Chemical/physical properties are summarized in the attached worksheet.

Lead Cyanide

Lead cyanide is a white crystalline material that is slightly soluble in aqueous solutions of ammonium salts, ammonium hydroxide, hot nitric acid, and alkali cyanides. It has been used to a small extent as an insecticide and in electroplating for producing a smutty effect in green gold deposits. It is not generally available commercially, but is best prepared for use by slowly adding, with stirring, a cold solution of sodium cyanide and sodium hydroxide to lead acetate dissolved in cold water. The precipitated lead cyanide is allowed to settle, washed and dried, if to be stored.[1433] Physical/chemical properties are summarized in the attached worksheet.

Nickel Cyanide

Nickel cyanide is a light green powder that is present either as the tetrahydrate, $Ni(CN)_3 \cdot 4\ H_2O$, or as $2\ Ni(CN)_2 \cdot 7\ H_2O$. It is hydroscopic but at 200 C becomes anhydrous. It reacts with alkali and alkaline earth cyanides to form soluble orange or yellow tetracyanonickelates. Nickel cyanide is usually prepared by the action of an alkali metal cyanide on a solution of a nickel salt.

Nickel cyanide is not used in electrodeposition of the metal, because nickel cannot be deposited from an aqueous solution of the pure alkali nickel cyanide complex. Nickel cyanide is added to plating baths for the electroplating of other metals such as gold or silver to make harder deposits, or in zinc-plating baths to enhance the brightness. It also is used in small quantities as an anticorrosion agent.[1433] It reacts with alkali metal and alkaline earth metal cyanides to form nickelocyanides.

Physical/chemical properties are summarized in the attached worksheet.

Potassium Cyanide

Potassium cyanide is a white, crystalline, deliquescent solid that is less subject to hydrolysis in aqueous solution than is sodium cyanide. Potassium cyanide is made either by neutralization of potassium hydroxide with hydrogen cyanide or by the Beilby process which utilizes the molten carbonate. The overall reaction is as follows:

$$K_2\ CO_3 + 4C + 2NH_3 \overset{\Delta}{\rightarrow} 2KCN + 3CO + 3H_2O$$

Potassium cyanide is often used in preference to sodium cyanide for electroplating silver and copper. The reasons for this preference are:

(1) the potassium bath can be operated over a wide current-density range;

(2) a lower metal content is required for a comparable current-density range and electrodeposit appearance;

(3) it has a greater tolerance to organic contaminants; and

(4) it permits higher carbonate concentrations. Potassium cyanide also finds some use in mixtures with sodium cyanide for nitriding steel.[1146]

Physical/chemical properties for potassium cyanide are summarized in the attached worksheet.

Silver Cyanide

Silver cyanide, AgCN or Ag_x $(CN)_x$, is a white odorless powder that has a complex structure. Silver cyanide reacts with solutions of soluble metal cyanides to form a very slightly dissociated complex union $[Ag(CN)_2]$. This complex is formed in the cyanidation of silver ores and in electroplating. The complex is decomposed by alkaline sulfides with precipitation of silver sulfide and by reaction with mineral acids with precipitation of silver cyanide and liberation of hydrogen cyanide.[1158]

Silver cyanide is usually manufactured by adding an alkali metal cyanide to a solution of silver nitrate according to the following reaction:

$$Ag\ NO_3 + Na\ CN \rightarrow Ag\ CN \downarrow + Na\ NO_3$$

The principle use of silver cyanide is in electroplating.

The physical/chemical properties for silver cyanide are summarized in the attached worksheet.

Sodium Cyanide

Sodium cyanide is a hard, white crystalline solid. At high temperatures, it does not ignite in contact with air; this permits its use in high temperature metal treatment. Its applications include metal treatment, electroplating baths and synthesis of organic intermediates. Its use in extraction of low-grade gold, silver and molybdenum ores account for only a small part of the total use.

Most sodium cyanide is manufactured either by the neutralization of hydrogen cyanide with sodium hydroxide or by the Castner Process described as follows:

1) Sodamide is formed from sodium and ammonia:

$$2NH_3 + 2Na \rightarrow 2Na\ NH_2 + H_2$$

2) Sodamide reacts with carbon at 350-400 C to form sodium cyanamide:

$$2\ Na\ NH_2 + C \rightarrow Na_2\ CN_2 + 2H_2$$

3) At temperatures of about 700 C, the sodium cyanamide reacts with further quantities of carbon to form molten cyanide:

$$Na_2\ CN_2 + C \rightarrow 2Na\ CN$$ [1433]

Physical/chemical properties for sodium cyanide are summarized in the attached worksheet.

Zinc Cyanide

Zinc cyanide is a white solid. It is very stable when dry and can be heated in the absence of air to 1000 C without decomposition. In the presence of air it decomposes at 800 C. It dissolves easily in solutions of soluble cyanides to form complexes such as:

$$K_2[Zn(CN)_4] \text{ and } Na_2\ [Zn(CN)_4] \cdot 3H_2O$$

Zinc cyanide is prepared by a number of processes. One involves its preparation from zinc oxide, sulfuric acid, and sodium cyanide according to the following equations:

$$ZnO + H_2\ SO_4 \rightarrow Zn\ SO_4 + H_2O$$

$$Zn\ SO_4 + 2NaCN \rightarrow Zn(CN)_2\downarrow + Na_2\ SO_4$$

It may also be prepared by treating a solution of zinc acetate with hydrogen cyanide. As a waste considerable zinc cyanide, as $Na_2[Zn(CN)_4]$, is formed in gold and silver ore processing with sodium cyanide.[1433]

The principal uses for zinc cyanide are in electroplating, and occasionally in medicine. Its physical/chemical properties are summarized in the attached worksheet.

2. TOXICOLOGY

Volatile cyanides resemble hydrocyanic acid physiologically, inhibiting tissue oxidation and causing death through asphyxiation. The non-volatile cyanide salts are of high toxicity systemically, if they are ingested. Care should be taken to prevent the formation of hydrocyanic acid. Daily exposure to cyanide solutions may cause a "cyanide" rash characterized by itching, and by muscular, papular, and vesicular eruptions. Exposure to small amounts of cyanide compounds over long periods of time may cause loss of appetite, headache, weakness, nausea, dizziness and symptoms of the upper respiratory track and eyes. The Threshold Limit Value (TLV) (ACGIH) recommended is 5 milligrams per cubic meter of air.

The toxicity of the various metal ions that combine with the cyanide ion has been extensively discussed in the report "Water Quality Criteria".[0536] Even if the cyanide ion concentration is reduced to near zero, the concentration of the metal ions remaining must be considered. Therefore, concentration limits have been established for the metallic ions in public water supplies. The permissible and desirable limits for cyanide and metal ions are summarized below.[0536]

Constituent	Permissible Criteria, mg/l	Desirable Criteria, mg/l
Cadmium	0.01	Absent
Copper	1.0	Virtually absent
Lead	0.05	Absent
Silver	0.05	Absent
Zinc	5	Virtually absent
Cyanide	0.20	Absent

Aquatic Toxicity

A discussion not only of cyanide ion toxicity but of the toxicity toward aquatic life of all the metal ions covered as cyanides in this Profile Report is also included in the report "Water Quality Criteria".[0536] The toxicity of cyanides towards aquatic life increases rapidly with a rise in temperature. Fish can recover from short exposure to concentrations of less than 1.0 mg/l of cyanide ion if removed to water free of cyanides. Fish appear to be able to convert cyanide to thiocyanate, an ion that is not inhibitory to their respiratory enzymes. The complex cyanides formed by the action of cyanide with zinc or cadmium salts are much more toxic than sodium cyanide. However, the reaction between cyanide and nickel produces a cyanide complex less toxic than sodium cyanide at high pH levels.

3. OTHER HAZARDS

Cyanides evolve hydrocyanic acid rather easily when acidified. HCN is a flammable gas and is highly toxic. Carbon dioxide from the air is sufficiently acid to liberate hydrocyanic acid from cyanide solutions.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Adequate procedures for safe handling and storage of cyanides as concentrated or dilute solutions are described in detail by Graham.[1562] His book provides recommended procedures for building design, equipment design, ventilation, employee safety, design of storage containers, and material specifications. The U. S. Department of Transportation (DOT) classification and shipping regulations for the various cyanides covered by this Profile Report are summarized below:

Compound	Shipping Regulations
Cadmium Cyanide	Cadmium cyanide is not normally prepared commercially in the dry form, but usually as a solution of sodium cyanocadmate, by dissolving cadmium oxide in sodium cyanide solutions. See "Sodium Cyanide".

Compound	Shipping Regulations
Calcium Cyanide	Calcium cyanide is shipped in steel drums as a Class B poison. It must be protected from moisture because it decomposes slowly. Also, it usually contains calcium carbide which will liberate acetylene upon contact with moisture.
Cuprous Cyanide	Cuprous cyanide is usually packed in fiber drums in wooden kegs. It is a toxic item and should carry warning labels as recommended by the Manufacturing Chemists Association. It may be shipped by freight express or motor truck but is not mailable.
Lead Cyanide	Lead cyanide is not usually manufactured on a large scale. It is shipped under the same regulations as cuprous cyanide.
Nickel Cyanide	Nickel cyanide is shipped as a Poison B under a poison label.
Potassium Cyanide	Potassium cyanide is shipped as a Poison B under a poison label.
Silver Cyanide	Silver cyanide is packed in cardboard tubes or in fiber containers. It may be shipped by express but is not mailable. It is a restricted item and must carry a warning label similar to that recommended by the Manufacturing Chemists Association.
Sodium Cyanide	Sodium cyanide is shipped in iron drums and smaller containers packed in drums. Container cars can also be used. Drums and packages are shipped under a poison B label. Carload shipments carry a placard labeled "Dangerous".
Zinc Cyanide	Zinc cyanide is shipped under the same regulations as cuprous cyanide.

A definition of acceptable criteria for disposal of cyanide salts must also take into account acceptable criteria for not only the release of cyanide ion but also the release of the associated metallic constituents into streams or sewage works. Most industrial states have laws regulating the discharge of waste streams from metal processing works and plating operations. Laws are being enacted that reduce the quantities of waste that may be discharged, but in many cases there are not definite standards for acceptable wastes. The severity of the waste nuisance varies with:

(1) Volume and toxicity of wastes produced (as metal ions free of cyanide).

(2) Nature of receiving waters,

(3) Minimum flow of the natural streams, or

(4) The process used in the sewage plant.

Graham[1562] includes information (Table 1) which compares the concentration of constituents in typical plating rinse wastes with standards set by some states. Future laws will lower the range of permissible concentrations.

The safe disposal of the metal cyanides is defined in terms of the recommended provisional limits for the residual metal cyanides and the disposal process product soluble metal ions in the atmosphere, in potable water sources, and in marine habitats. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Cadmium cyanide	0.002 mg/M^3 as Cd	0.01 TLV
Calcium cyanide	0.05 mg/M^3 as CN	0.01 TLV
Copper cyanide	0.01 mg/M^3 as Cu	0.01 TLV
Lead cyanide	0.0015 mg/M^3 as Pb	0.01 TLV
Nickel cyanide	0.01 mg/M^3 as Ni	0.01 TLV
Potassium cyanide	0.05 mg/M^3 as CN	0.01 TLV
Silver cyanide	0.0001 mg/M^3 as Ag	0.01 TLV
Sodium cyanide	0.05 mg/M^3 as CN	0.01 TLV
Zinc cyanide	0.05 mg/M^3 as CN	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Cadmium cyanide	0.01 mg/l as CN	Drinking Water Standard
Calcium cyanide	0.01 mg/l as CN	Drinking Water Standard
Copper cyanide	0.01 mg/l as CN	Drinking Water Standard
Lead cyanide	0.01 mg/l as CN	Drinking Water Standard
Nickel cyanide	0.01 mg/l as CN	Drinking Water Standard
Potassium cyanide	0.01 mg/l as CN	Drinking Water Standard
Silver cyanide	0.01 mg/l as CN	Drinking Water Standard
Sodium cyanide	0.01 mg/l as CN	Drinking Water Standard
Zinc cyanide	0.01 mg/l as CN	Drinking Water Standard

TABLE 1

CONCENTRATION OF CONSTITUENTS OF TYPICAL DILUTE PLATING RINSE WASTES COMPARED WITH SOME STATE STANDARDS[1562]

Plating Wastes			Range of Permissible Concentration,ppm		
Constituent	Concentration, ppm (Avg)	(Max)	Effluent to Streams	In Streams	Influent* to Sewage Works
CN	30	500	None to 0.5	None to 0.2	2
Cu	20	100	1	0.4	1 - 3
Zn	15	50	-	0.3 - 1.5	-
Cd	15	50	-	0.3	-
Ni	25	200	-	-	1 - 3
Pb	0	30	-	0.35	0.1
pH	Varies	Varies	6.5-9.5	6.3 - 9	5 - 6.5

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* Influent after dilution and mixing with all other wastes.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Much of the information in the literature on the volume and composition of electroplating, metal treating, metal finishing wastes, and mining wastes refers to the large or intermediate-size plants that do routine operations. There are wide variations in both volume and composition from plant to plant. This is because the waste streams from these plants are the product of local plant conditions and practices such as dragout, rinsing techniques, recovery methods employed, and the admixture of other waste streams. There is little or no information on the volume and composition of wastes encountered in the smaller plating shops that do general plating.[0783]

Recovery and Conservation of Water and Cyanide

Any expedient that prevents the loss of chemicals or removes them from the waste stream in reusable or resalable form may be considered as a recovery operation. In recovery processes the metal ion can be recovered as well as sodium cyanide. In some localities water is valuable and its recovery may be economically attractive.

Evaporation Methods. The evaporation of collected plating rinses for return to plating baths is an attractive process. Cyanide wastes have been concentrated (by distillation of H_2O) to recover the metal and cyanide values for reuse in the plating process. The distillate generated is used as rinse water. In many cases the recovery of the cyanides by this technique is economically feasible when the values of the cyanides and water are considered.[1562] When feasible, this method is recommended because resources are conserved and landfill is not required for disposal.

Ion-Exchange Methods. Ion exchange has been successfully applied to mixed wastes (chromium and cyanides) by the use of a duel bed process. In this process the waste stream is first passed through a cationic exchanger to absorb metals, help break up complex metal cyanides and generate free hydrogen cyanide, and then through an anionic exchanger to absorb the liberated hydrogen cyanide.[0783] The concentration of cyanide in the waste stream must be below about 5 percent. Regeneration--the removal of cyanides and metals from the resins--must be done periodically. The is accomplished by passing sulfuric acid and/or sodium hydroxide through the resins to redissolve the cyanides and metals. Regenerated solutions are generally concentrated but still toxic. If they are to be discharged, they require chemical treatment, but because they are concentrated treatment may be carried out batchwise in small tanks. In many cases recovery of the metals as cyanide is economically feasible.

Chemical Recovery Methods. Chemical recovery methods are not widely used, except for precious metals. In plating, metal treating, or mining the precious metals are nearly always recovered. Silver is plated from cyanide solutions or precipitated by the addition of zinc dust.[1562] Copper is precipitated from cyanide solutions by the addition of hydrazine.[0783] Nickel and copper are precipitated at elevated temperatures at a pH above 3.5 by the addition of iron.[0783]

Waste - Plus - Waste Method. George and Cochran[1112] describe a method for the recovery of six metal cyanides. Addition of an acid waste to an alkaline cyanide waste was investigated for five different combinations of cyanide wastes. At the optimum final pH values of the mixtures, the metal cyanides were almost quantitatively precipitated. The pH was adjusted by the addition of acid rinse water and lime. No evolution of hydrogen cyanide was detected. The waste-plus-waste technique, though not in commercial use, is attractive because no reagents for recovery are required of the metal cyanides and the effluent may be treated to reduce residual cyanide content via chlorination or electrolytic oxidation.

Cyanide Destruction

The chemical destruction of cyanides in liquid waste streams has received a great deal of attention and numerous methods have been proposed. Some of the more attractive methods are briefly discussed in the following paragraphs. For dilute cyanide wastes, chlorination under alkaline conditions is generally favored; too much heat is generated if the technique is used on concentrated wastes and undesirable and dangerous side-reactions will take place unless the operation is carried out very slowly, or the waste is first diluted. When considerable amounts of concentrated wastes must be treated, e.g., from cyanide heat-treating, the wastes must be diluted or another method for cyanide destruction such as electrolytic oxidation must be used.

Chlorination. Oxidation of cyanides by the hypochlorite ion (which may be furnished by either chlorine or sodium or calcium hypochlorite) proceeds in three stages.[1562,0586]

$$CN^- + H^+ + OCl^- \rightarrow CNCl + OH^- \quad (1)$$

$$CNCl + 2OH^- \rightarrow CNO^- + Cl + H_2O \quad (2)$$

$$2CNO^- + 3OCl^- + H_2O \rightarrow 2CO_2 + N_2 + 3Cl^- + 2OH^- \quad (3)$$

Reaction (1) is very fast; reaction (2) is very slow below pH 9 unless excess hypochlorite is present; at pH 10 or higher it is rather rapid and oxidation to the cyanate stage is complete in 5 minutes or less, provided no nickel ion is present. If nickel is present, reaction (2) is not completed in less than 30 minutes, and then only if 20 percent excess reagent is used. Reaction (3) is very slow above pH 9 requiring at least an hour, and many hours if the pH is 11 or more. The best practice is to adjust the pH to 8.5 and allow 1 hour reaction time. About 10 percent excess hypochlorite should be used, or destruction of the cyanides will be incomplete.

The heavy metals present will be precipitated as hydroxides or carbonates in total chlorination treatment. An exception is copper which will not be precipitated in wastes containing copper and rochelle salts unless sufficient calcium is also present as chloride or hydroxide, so that the tartrate will be precipitated as the calcium salt, thus allowing precipitation of copper. It has been shown that iron cyanide complexes are not destroyed by chlorination and that a cyanide residual reappears on long standing (100 hours).

Total chlorination (i.e., to N_2 and CO_2) does not lend itself readily to continuous treatment processes because current control methods are not adequate. If a packaged cyanide treatment system is employed, continuous operation for oxidation to cyanate (1,000 times less toxic than cyanide) is possible.[1309] A second system is required for oxidation of cyanates, with appropriate holding time due to the slow reaction.

Kastone Process. DuPont has introduced a process which appeals primarily to small plant operators using cyanide baths to plate zinc or cadmium. This process oxidizes cyanides to cyanates and simultaneously precipitates zinc or cadmium complexes by simple filtration. The Kastone Process uses a proprietary peroxygen formulation that contains 41 percent hydrogen peroxide with trace amounts of stabilizers.[0484,0485] The cyanates, though 1,000 times less toxic than cyanides, cannot be discharged into most natural streams. Therefore, this process has only limited application.

Electrolytic Oxidation. Automatic electrolytic oxidation units are marketed by Research Control, Inc., for complete decomposition of cyanide ion content in waste streams.[0485] Some difficulties have been reported with this unit for dilute solutions, but this problem has been circumvented by using a semiconductive bed in the cell. The bed serves as an intermediate electrode that provides in effect more than a million anode and cathode sites per cubic foot.

Radiation Decomposition. A patent has been issued for destroying cyanides by gamma radiation which serves to rupture the $C\equiv N$ triple bond and converts the cyanide ion into harmless by-products.[0287] This method is not in commercial use at present.

Conversion of Cyanides to Ferrocyanide by Ferrous Sulfate. The formulation of less toxic cyanide complexes such as ferro and ferricyanides has been used as a method for disposing of cyanide waste waters. This process involves the use of iron salts to form complex compounds with the free cyanide in the wastes. These cyanide complexes are precipitated and removed as sludge. The major advantage of this treatment method is that it is relatively inexpensive where waste ferrous sulfate is available. However, considerable quantities of sludge are formed, and the treated solutions are strongly colored. There is also evidence that ferrocyanides may decompose to free cyanide in the presence of sunlight. The regeneration of cyanide can then contaminate the receiving stream.[0783]

Reaction with an Aldehyde. A patent has been issued for the removal of cyanide from a waste stream by reaction with an excess of an aldehyde according to the following[1791]:

$$KCN + CH_2O \text{ (aqueous)} + H_2O \rightarrow HOCH_2CN + KOH$$

$$CNCH_2OH + KOH + H_2O \rightarrow HOCH_2COOK + NH_3$$

It is claimed that nearly all cyanides, even stable complexes, are destroyed in this manner. However, though the reaction products are not toxic, there is the problem of disposal of the organic compounds formed.

Ozonation. Ozonation is reported to be more economical and easier to control than chlorination. Ozonation, however, oxidizes cyanides only to the cyanate in accordance with the reaction given below.

$$3CN^- + O_3 \rightarrow 3CNO^-$$

The oxidation of the cyanate is too slow to be practical.[1562]

Acidification. Waste acid solutions have been used to acidify cyanide waste solution. Air is then passed through the solution and the liberated hydrogen cyanide is discharged up a high stack or is passed through a burner. This method is not recommended because of the danger involved.

Lagooning. Though the methods discussed above are available for treating cyanide wastes, lagooning of cyanide wastes from small and medium sized metal processing and plating operations is widely practiced. For example, in the Los Angeles area commercial waste disposal companies collect cyanide wastes and truck these wastes to a large abandoned rock quarry. If precious metals, such as silver, are present, these are first removed by salvage companies.

The use of lagoons for cyanide wastes cannot be recommended because the cyanides may some day leak into underground water supplies and the wastes, if acidified, will liberate hydrogen cyanide.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The oxidation of cyanides in alkaline solution by chlorine or hypochlorites is an acceptable method for destroying cyanide. However, because cyanide wastes are generated by a large number of metal treating operators, some of whom are small, in some cases proper treatment is an economic burden and not always complete. It is, therefore, recommended that National Disposal Sites have the capability for treatment of cyanide wastes by the use of the chlorination techniques.

Additional research is recommended to establish operations that will permit recovery of the various metals, and either recovery or destruction of the cyanide. A study is also recommended of the economics associated with the various recovery methods proposed or now in use .

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Cadium Cyanide (84)

IUC Name Cadium cyanide

Common Names

Structural Formula

$Cd(CN)_2$

Molecular Wt. 164.45 Melting Pt. 7200 decomposes Boiling Pt.

Density (Condensed) 2.226 @ 20 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 1.71 at 15 C Hot Water Ethanol sl sol

Others: Alkali cyanide or hydroxide solutions

Acid, Base Properties

Highly Reactive with

Compatible with Most metals

Shipped in

ICC Classification Poison B < 200 lb. Coast Guard Classification Poison B Label

Comments Used in bright copper electroplating.
Readily forms complex cyanides.

References (1) 1433

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Calcium cyanide (91)

IUC Name Calcium cyanide

Common Names "Black cyanide"

Structural Formula

$Ca(CN)_2$

Molecular Wt. 92.12 Melting Pt. 1840 C(1) Boiling Pt. -

Density (Condensed) @ Density (gas) - @

Vapor Pressure (recommended 55 C and 20 C)

- @ - @ @

Flash Point - Autoignition Temp.

Flammability Limits in Air (wt %) Lower - Upper -

Explosive Limits in Air (wt. %) Lower - Upper -

Solubility

Cold Water Partial hydrolysis Hot Water Ethanol

Others:

Acid, Base Properties In water becomes alkaline due to hydrolysis

Highly Reactive with Weak acids to give HCN, decomposes in moist air. Solution alkaline. Reacts with CO_2 of air.

Compatible with

Shipped in 4 oz to 100 lb metal container

ICC Classification Poison label Class B poison Coast Guard Classification

Comments Article of commerce contains 40-50% $Ca(CN)_2$

References (1) 1433

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Copper cyanide (120)

IUC Name Cupric cyanide

Common Names

Structural Formula

$Cu(CN)_2$

Molecular Wt. 115.61 Melting Pt. Decomposes Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Insol. Hot Water - Ethanol sol.

Others: Soluble in acids or bases, sol in cyanide solution

Acid, Base Properties

Highly Reactive with Acid to give HCN. Not stable, can be dried.

Compatible with

Shipped in Glass bottles, special drums.

ICC Classification None. Coast Guard Classification

Comments

Not normally an item of commerce.

References (1) 1433

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Cuprous cyanide (128)

IUC Name Cuprous cyanide

Common Names

Structural Formula

CuCN

Molecular Wt. 89.56 Melting Pt 474 C Boiling Pt.

Density (Condensed) 2.92 @ 20 C(2) Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

- @ -   - @ -   @

Flash Point   Autoignition Temp.

Flammability Limits in Air (wt %) Lower - Upper -

Explosive Limits in Air (wt. %) Lower - Upper -

Solubility

Cold Water Insol Hot Water Insol Ethanol Insol

Others: Sol in NH_4OH, alkali cyanide solutions

Acid, Base Properties None

Highly Reactive with Decomposed by HNO_3 and dil HCl.

Compatible with Metals, glass

Shipped in 100-lb drums

ICC Classification None Coast Guard Classification

Comments

References (1)

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Lead cyanide (239)

IUC Name Lead cyanide

Common Names

Structural Formula

$Pb(CN)_2$

Molecular Wt. 259.23 Melting Pt. decomp. Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water slightly soluble Hot Water Ethanol

Others: decomposes in acid; soluble in NaCN solution

Acid, Base Properties

Highly Reactive with acids

Compatible with

Shipped in wooden kegs, fiber drums

ICC Classification none Coast Guard Classification none

Comments used in metallurgy

References (1) 1433

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nickel cyanide (295)

IUC Name Nickel cyanide

Common Names

Structural Formula

$Ni(CN)_2$

Molecular Wt. 182.81 Melting Pt. losses H_2O @200 C Boiling Pt. decomposes

Density (Condensed) 146.8 @ 20 C Density (gas) - @

Vapor Pressure (recommended 55 C and 20 C)

- @ - @ - @

Flash Point - Autoignition Temp. -

Flammability Limits in Air (wt %) Lower - Upper -

Explosive Limits in Air (wt. %) Lower - Upper -

Solubility

Cold Water Insol. Hot Water Ethanol

Others: Slight sol. in dil acid, freely in alkali cyanide, ammonia and ammonium carbonate.

Acid, Base Properties

Highly Reactive with acids.

Compatible with

Shipped in Wooden kegs, glass bottles, fiber drums, paper sacks.

ICC Classification Poison Label. Poison B<200lb Coast Guard Classification Poison Label Poison B (2)

Comments Used in nickel plating. Commercial salt usually contains 20-25% water.

References (1) 1433

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Potassium cyanide (344)

IUC Name Potassium cyanide

Common Names

Structural Formula

KCN

Molecular Wt. 65.11 Melting Pt. 634 C Boiling Pt. -

Density (Condensed) 1.52 @ 20 C Density (gas) - @ -

Vapor Pressure (recommended 55 C and 20 C)

- @ - @ - @ -

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower - Upper -

Explosive Limits in Air (wt. %) Lower - Upper -

Solubility

Cold Water 33 gm/100 ml Hot Water 50 gm/100 ml at 100 C Ethanol 50 gm/100 ml

Others:

Acid, Base Properties Strongly alkaline in aqueous solution, pH of 0.1N aq.soln. = 11.0

Highly Reactive with CO_2 in air, acids, metal salts, oxidizers

Compatible with most metals at room temperature

Shipped in

ICC Classification Poison B, Poison label Coast Guard Classification Poison B, Poison label

Comments Article of commerce, 95% KCN

References (1) 1433

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Silver cyanide (370)

IUC Name Silver cyanide

Common Names

Structural Formula

AgCN

Molecular Wt. 133.90(1)

Melting Pt. 320 C dec.(1)

Boiling Pt.

Density (Condensed) 3.95 @ 20 C

Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

- @

- @

- @

Flash Point

Autoignition Temp.

Flammability Limits in Air (wt %) Lower - Upper -

Explosive Limits in Air (wt. %) Lower - Upper -

Solubility

Cold Water Insol. Hot Water Insol. Ethanol Insol.

Others: Insol. dil. acids, sol. in alkali cyanides

Acid, Base Properties

Highly Reactive with Darkens on exposure to air. HCl releases to HCN.

Compatible with

Shipped in

ICC Classification Poison B, Poison Label

Coast Guard Classification Poison B
Poison label

Comments

References (1) 1433

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Sodium cyanide (387)

IUC Name Sodium cyanide

Common Names

Structural Formula

NaCN

Molecular Wt. 49.02 Melting Pt. 560 C Boiling Pt. 1500 C

Density (Condensed) 1.60(cubic) @ 20 C Density (gas) - @

Vapor Pressure (recommended 55 C and 20 C)

0.76 mmHg @ 800 C(1) 3.34 @ 900 C (1) 36 mmHg @ 100 C()

Flash Point - Autoignition Temp. -

Flammability Limits in Air (wt %) Lower - Upper -

Explosive Limits in Air (wt. %) Lower - Upper -

Solubility

Cold Water 32.8 gm/100 ml at 10 Hot Water 45 gm/100 ml at 34.7 C(1) Ethanol sl. sol.

Others: V. sol in lq. NH_3

Acid, Base Properties Strongly alkaline.

Highly Reactive with When heated in presence of traces of Fe or Ni decomposes. Air reacts with molten NaCN. Is a good reducing substance. Reacts with acids to liberate HCN.

Compatible with most materials of construction.

Shipped in 25 lb packages, 100, 160, 200 lb drums

ICC Classification Poison Class B Coast Guard Classification Poison Class B

Comments Sold as 30% soln, 73-75%, 96-98% briquettes, granular

References (1) 1433

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Zinc cyanide (457)

IUC Name Zinc cyanide

Common Names

Structural Formula

$Zn(CN)_2$

Molecular Wt. 117.42 Melting Pt. Decomp. 800 C Boiling Pt. -

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.00058g/100g @18 C Hot Water Ethanol Insoluble

Others: Soluble in dilute mineral acids.

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Poison B - Poison Label Coast Guard Classification Poison B

Comments

References (1) 1433